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OF
INORGANIC CHEMISTRY

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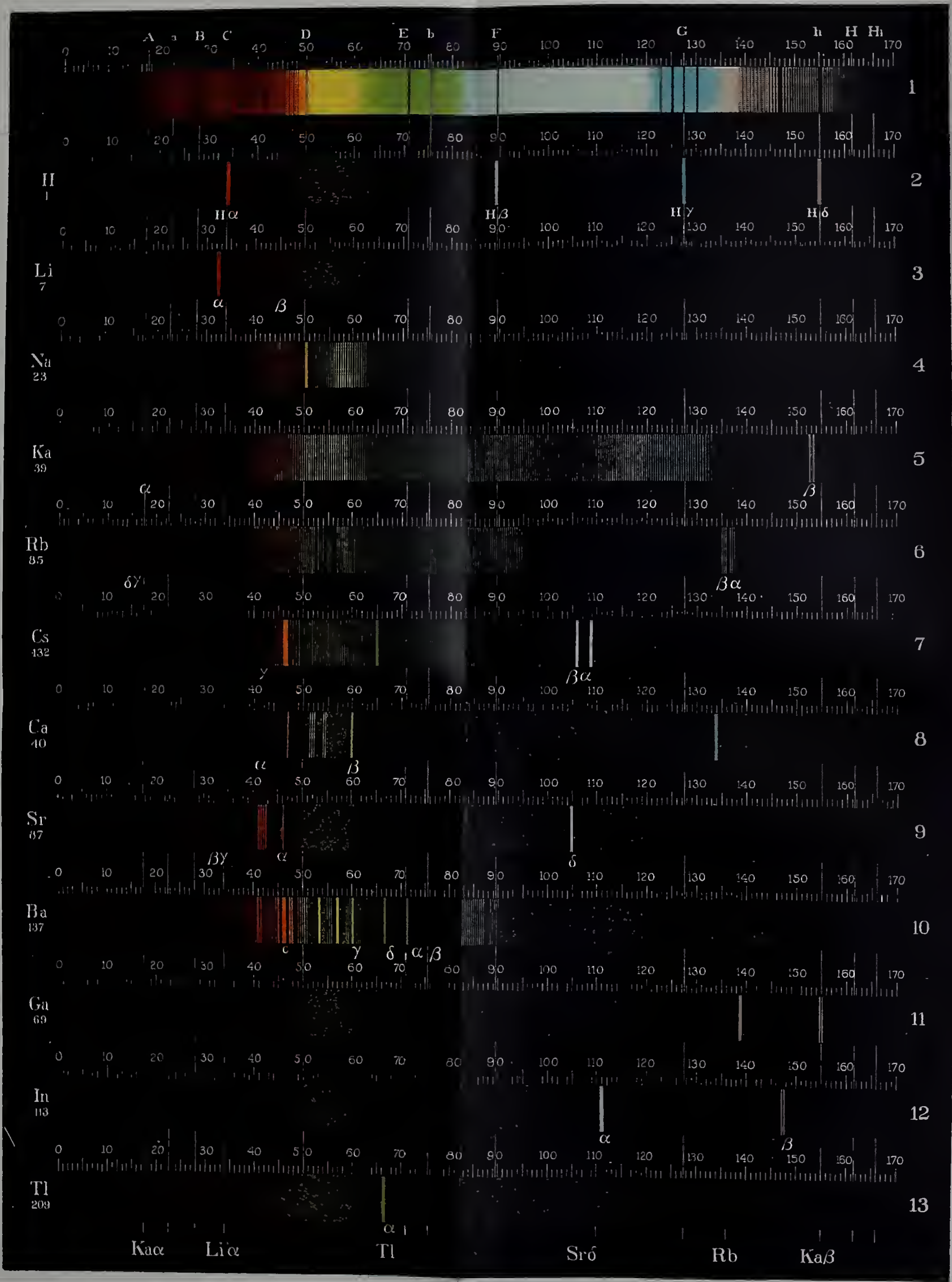
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Ca 40
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Sr 87
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Ba 137
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Ga 69
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In 113
12
α β
Tl 203
13
α
Kaα Liα Tl Srδ Rb Kaβ

A TEXT-BOOK OF INORGANIC CHEMISTRY.

BY

PROF. VICTOR VON RICHTER,

UNIVERSITY OF BRESLAU.

AUTHORIZED TRANSLATION,

BY

EDGAR F. SMITH,

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF PENNSYLVANIA,
PHILADELPHIA.

FOURTH AMERICAN FROM THE SIXTH
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PREFACE

TO THE

FOURTH AMERICAN EDITION.

In its present form this volume represents a translation of the sixth German edition. The inductive method adopted in previous editions has been continued. The changes that will be observed throughout the text consist mainly of corrections and additions made necessary by the most recent investigations. It may be added that as three years have passed since the publication of the German edition, the translator has taken the liberty of introducing here and there such new matter as the present state of chemical science has seemed to demand.

PREFACE

TO THE

THIRD AMERICAN EDITION.

THE present edition contains a rather extended section upon the thermal behavior of bodies, and throughout the work frequent occasion is taken to call attention to the dynamical side of chemical reactions. The sections upon the pressure and condensation of gases, and that upon the dissociation phenomena, have also been considerably increased, while new facts relating to the elements and their derivatives, to their preparation, etc., have been introduced in their proper places. The leading and characteristic features of the preceding editions remain unchanged.

PREFACE

TO THE

SECOND AMERICAN EDITION.

THE present edition is a translation of the fourth German edition. Many parts of the work have been rewritten, and new matter incorporated. The features which recommended the previous edition have been preserved, and as now presented it is hoped that the work may continue to be of service to the student of chemical science.

The translator would here express his obligations to Mr. Allen J. Smith, who has read the entire proof, revised the index and table of contents, as well as rendered other valuable assistance.

PREFACE

TO THE

FIRST AMERICAN EDITION.

THE success of PROF. VON RICHTER'S work abroad would indicate its possession of more than ordinary merit. This we believe true, inasmuch as, in presenting his subject to the student, the author has made it a point to bring out prominently the relations existing between fact and theory. These, as well known, are, in most text-books upon inorganic chemistry, considered apart, as if having little in common. The results attained by the latter method are generally unsatisfactory. The first course—that adopted by our author—to most minds would be the more rational. To have experiments accurately described and carefully performed, with a view of drawing conclusions from the same and proving the intimate connection between their results and the theories based upon them, is obviously preferable to their separate study, especially when they are treated in widely removed sections or chapters of the same book. Judging from the great demand for VON RICHTER'S work, occasioning the rapid appearance of three editions, the common verdict would seem to be unanimously in favor of its inductive methods.

In the third edition, of which the present is a translation, the Periodic System of the Elements, as announced by MENDELEJEFF and LOTHAR MEYER, is somewhat different, in the manner of development and presentation, from that appearing in the previous editions. This was done to give more prominence to and make more general the interesting relations disclosed by it. Persons examining this system carefully will be surprised to discover what a valuable aid it really has been, and is yet, in chemical studies. Through it we are continually arriving at new relations and facts, so that we cannot well hesitate any longer in adopting it into works of this character. It is, indeed, made the basis of the present volume. In accordance with it, some change in the treatment of the metals, ordinarily arbitrarily considered, has been made.

A new feature of the work, and one essentially enlarging it, is the introduction of the thermo-chemical phenomena, briefly presented in the individual groups of the elements and in separate chapters, together with the chemical affinity relations and the law of periodicity. "Hereby more importance is attributed to the principle of the greatest heat development than at present appears to belong to it, because it was desired, from didactic considerations, by the explanation of the few anomalies, to afford the student the incentive and opportunity of deductively obtaining the majority of facts from the thermal numbers, on the basis of a simple principle. To facilitate matters, there is appended to the volume a table containing the heat of formation of the most important compounds of the metals."

Trusting that the teachings of this work will receive a hearty welcome in this country, and that they will meet a want felt and often expressed by students and teachers, we submit the following translation of the same.

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INTRODUCTION.

SPECIAL PART.

THE METALS.

A TEXT-BOOK

OF

INORGANIC CHEMISTRY.

INTRODUCTION.

The study of Nature reveals an endless multitude of objects or *bodies*. That which forms the basis of the latter, strongly characterized by extent and weight, we designate *substance* or *matter*. The investigation of the internal and external structure of bodies, their classification according to conformable or distinguishing characteristics, constitute the task of the descriptive sciences; of mineralogy, of geology, of descriptive botany and zoölogy, of anatomy, etc.

A closer scrutiny of natural objects discloses the fact that they in time succumb to many more or less serious alterations or changes. We observe that minerals form, crystallize, or disintegrate and crumble to pieces; that plants and animals spring up, grow, and then fall into decay and decomposition. Such changes in the condition of bodies occurring with time are entitled *phenomena*. The investigation of these during their progression, the determination of the laws according to which they occur, the explanation of the causes underlying them, form the task of the *speculative sciences*, physics and chemistry—depending upon the nature of the phenomena.

Like every other classification or definition, the division of the natural sciences into *speculative* and *descriptive* is not strictly correct. It does not completely cover the nature of the phenomena. We approximate the actual facts more closely by designating the natural sciences as *general* and *special*. The general sciences, mechanics, physics, and chemistry, occupy themselves with the study of the general properties and transformations of bodies, regardless of the external form, and deal chiefly with their substance only. Special branches—like botany and zoölogy—consider distinct classes of bodies, first in reference to their form (morphology, etc.), and afterward in relation to their transformations and alterations. Physiology of animals and plants, and geology, investigate the physical and chemical phenomena of particular classes of bodies, and are, therefore, speculative sciences. On the other hand, chemistry is also a descriptive science, inasmuch as it considers the external properties of chemical substances.

Although no abrupt boundaries are presented in Nature, but gradual transitions and intermediate steps throughout, two tolerably distinct classes of phenomena may be observed. Some changes in the condition of bodies are only superficial (external), and are not accompanied by material alteration in substance. Thus heat converts water into steam, which upon subsequent cooling is again condensed to water, and at lower temperatures becomes ice. In these three conditions, the solid, liquid, and gaseous, the *substance* or the *matter* of water or ice is unchanged; only the separation and the motion of the smallest particles—their states of aggregation—are different. If we rub a glass rod with a piece of cloth, the glass acquires the property of attracting light objects, *e.g.*, particles of paper. It becomes electrified. An iron rod allowed to remain suspended vertically for some time slowly acquires the power of attracting small pieces of iron. Through the earth's magnetism it has become magnetic. In both instances the glass and iron receive new properties; in all other respects, in their external and internal form or condition, they have suffered no perceptible alteration; the glass is glass, and the iron remains iron. All such changes in the condition of bodies, unaccompanied by any real alteration in substance, are known as *physical phenomena.*

Let us turn our attention now to the consideration of another class of phenomena. It is well known that ordinary iron undergoes a change, which we term *rusting*, *i. e.*, it is transformed into a brown substance which is entirely different from iron. On mixing finely divided copper filings with flowers of sulphur (pulverulent sulphur) there results an apparently uniform, grayish-green powder. If this be examined, however, under a magnifying glass, we can very plainly distinguish the red metallic copper particles in it from the yellow of the sulphur; by treating with water, the specifically lighter sulphur particles can easily be separated from those of the copper. Carbon disulphide will also dissolve out the sulphur particles. Hence this powder represents nothing more than a *mechanical mixture.* If, however, this mixture be heated, *e. g.*, in a glass test-tube, it will commence to glow, and on cooling, a black, fused mass remains, which differs in all respects from copper and sulphur, and even under the strongest microscope does not reveal the slightest trace of the latter, and elutriation with water or treating with carbon disulphide will not effect a separation of the ingredients. By the mutual action of sulphur and copper in presence of heat, a new body with entirely different properties has been produced, and is named copper sulphide. Mixtures of sulphur with iron or with other metals act in a similar manner; and the resulting bodies are known as sulphides.

Such mutual action of different bodies occurs not only under the influence of heat, but frequently at ordinary temperatures. If, *e. g.*, mercury and sulphur are rubbed continuously in a mortar, there is produced a uniform, black compound, called mercury sulphide. The action of gaseous chlorine upon various metals is quite energetic. When finely divided antimony is shaken into a flask filled with yellow chlorine gas, flame is produced; each antimony particle burns in the chlorine with a bright white light. The product of this action of solid metallic antimony and gaseous yellow chlorine is a colorless, oily liquid, known as antimony chloride. Such occurrences, therefore, in which a complete and entire alteration takes place in the bodies entering the reaction, are termed *chemical phenomena. Chemistry, then, is that department of natural science which occupies itself with the study of those phenomena in which an alteration of substance has occurred.*

In the previously described experiments we observed the phenomena of *chemical combination;* from two different bodies arose new homogeneous ones. The opposite may occur, consisting in the *decomposition* of compound bodies into two or more *dissimilar* ones. If red mercuric oxide be heated in a test-tube, it will disappear; a gas (oxygen) is liberated, which will inflame a mere spark on wood; in addition, we find deposited upon the upper, cooler portions of the tube, globules of mercury. From this we observe that on heating solid red mercuric oxide two different bodies arise; gaseous oxygen and liquid mercury. We conclude, then, that mercuric oxide holds in itself, or consists of, two constituents—oxygen and mercury. This conclusion, arrived at by decomposition, or *analysis*, may be readily verified by combination or *synthesis*. It is only necessary to heat mercury for some time, at a somewhat lower temperature than in the preceding experiment, in an atmosphere of oxygen, to have it absorb the latter and yield the compound we first used—red mercuric oxide. The direct decomposition of a compound body into its constituents by mere heat does not often happen. Generally, the coöperation of another substance is required, which will combine with one of the constituents and set the other free. In this manner we can, for example, effect the decomposition of the previously synthesized mercury sulphide, viz., by heating it with iron filings; the iron unites with the sulphur of the mercury sulphide, to form iron sulphide, while the mercury is set free.

If, in a similar manner, natural objects be decomposed, bodies or substances are finally reached which have withstood all attempts to bring about their division into further constituents, and which cannot be formed by the union of others. Such substances are *chemical elements;* they cannot be converted into each other, but constitute, as it were, the limit of chemical change. Their number, at present, is about 70; some have been only recently discovered. To them belong all the metals, of which iron, copper, lead, silver, and gold are examples. Other elements do not possess a metallic appearance, and are known as *metalloids.* It would be more correct to term them *non-metals.* To these belong sulphur, carbon, phosphorus, oxygen, etc. The line between metals and non-metals is not very marked.

When the elements unite with each other in smaller or larger numbers they produce the compound bodies known to us. Water is a compound of two gaseous elements—hydrogen and oxygen; common salt consists of the metal sodium and the gas chlorine. The elements make up not only our own earth, but the heavenly bodies are composed of them; at least as far as has been proved by spectrum analysis.

THE PRINCIPLE OF THE INDESTRUCTIBILITY OF MATTER.

If the quantities by weight of substance entering into a chemical change be determined, we notice that in all transpositions, in the decomposition of a compound into its constituents, and in the union of the elements to form compound bodies, loss in weight never occurs. *The weight of the resulting compounds is invariably equal to the sum of the weights of the bodies entering the reaction.* Well-known, general phenomena apparently contradict this scientific conclusion. We observe plants springing from a small germ and constantly acquiring weight and volume. This spontaneous increase of substance, however, is only seeming. Closer inspection proves conclusively that the growth of plants occurs only in consequence of the absorption of substance from the earth and atmosphere. The opposite phenomenon is seen in the burning of combustible substances, where an apparent annihilation of matter takes place. But even in this, careful observation will discover that the combustion phenomena consist purely in a transformation of visible solid or liquid bodies into non-visible gases. Carbon and hydrogen, the usual constituents of combustible substances, *e.g.*, a candle, combine in their combustion with the oxygen of the air and yield gaseous products—the so-called carbon dioxide and water—which diffuse themselves in the atmosphere. If these products be collected, their weight will be found not less, but indeed greater, than that of the consumed body, and this is explained by the fact that in addition to the original weight they have had the oxygen of the air added.

From what has been remarked we can conclude that in chemical transpositions loss in matter does not occur, nor is there a new creation of the same observed. Compounds are formed and disappear, because they are converted into new forms, but their substance (matter), their weight, does not disappear, and is not produced anew. This fundamental truth is called the *principle of the indestructibility of substance* (*matter*). Lavoisier, in the eighteenth century, first established it by convincing experiments. Combined with the principle of the conservation of energy, it constitutes the firm foundation of all scientific knowledge.

THE PRINCIPLE OF THE CONSERVATION OF ENERGY—CHEMICAL ENERGY.

Causes underlie and influence all material phenomena. The final cause of phenomena we term *force*, accepting for the various sorts of phenomena a variety of forces. Some of these are attraction and repulsion, light, heat, electricity, cohesion, chemical affinity. These names, however, only represent kinds of phenomena, without explaining their true nature. Of the nature of some of these forces we know, positively, that they consist of various modes of motion of portions of matter. In the case of mechanical force it is obvious that it depends solely upon the motion of masses; but other forces are nothing more than modes of motion. The phenomena of light are explained by the very rapid movements of the smallest particles, and these act upon the eye through the aid of a gaseous medium—ether. The phenomena of heat are due to the less rapid motion of weighable portions of matter which affect our sense of feeling. Accurate physical investigations have established that the different forces or modes of motion can *never* be destroyed, but only transferred from one body to others, and changed from one kind to another. The movements or vibrations of one variety pass into those of another. For example, a discharged bullet is heated by coming in contact with any obstruction in its course; the visible motion of the entire mass in this instance is transformed into the invisible motions of the smallest particles, and appears as heat. The heat motions can, on the other hand, be again changed into mechanical motion (molecular motion), or into light, magnetism, or electricity.

In all these transformations of the different modes of motion into one another, we observe a perfect equivalence of their quantity. If a mass motion, whose quantity is designated as mechanical work, can produce a certain degree of heat, so *vice versa*, the latter can perform the same mechanical work (the mechanical equivalent of heat, light, electricity). Upon this *equivalence of transformation* rests the *principle of the conservation of force or energy*, according to which the various forces or motions of *matter* can neither be annihilated nor produced anew. This principle, forming one of the most important corner-stones of natural science, was first sharply defined by the speculative observations of Dr. J. R. Mayer, of Heilbronn, in 1842, and since then has been repeatedly confirmed by experiment.

The most recent advance in physics has led to the negation of the objective existence of all abstract physical forces. Not considering the phenomena of electricity and those of chemical affinity—the reduction of which to forms of motion is clearly foreseen, and not to be doubted—the only remaining enigmatical force is that of attraction or gravity. To affirm the existence of gravity is nothing more than to give expression to the fact that bodies in space tend to approach each other. The supposition that the active cause of gravity existed within the bodies themselves, was long ago discarded by Newton as "*absurdum;*" it is merely a mathematical fiction. The action of a body in a place where it does not exist, without the aid of a medium, is inconceivable. The transference of the gravitation into material bodies, further contradicts the principle of conservation of energy, as gravity is neither transferred nor exhausted—whether it be through the approach of bodies, whereby the force always increases—or by planet movement, in which the centrifugal component is constantly overcome. Therefore, the active cause of gravity is not to be sought after in bodies themselves, but without them, and, indeed, in a substantial medium—ether—without the acceptance of which natural investigation cannot proceed.

If we desire to make a preliminary presentation upon these relations, the following would be the simplest and most probable: Space is filled by the smallest possible material particles, but as they are all alike, they do not possess gravity, and are found in constant transferable motion—*ether substance.* By the congress of the smallest ether particles to mass-aggregates arise the chemical elementary atoms, which constitute material bodies—*substance or matter.* If, now, in addition to this *one* mass-aggregate, a second appear in space, an effort to approach each other produced by the action (collision) of the disturbed ether surrounding them, will appear—they possess gravity. By these suppositions the obscure ideas upon potential energy and energy of place are removed. A much clearer and more distinct presentation and confirmation of these representations, especially as regards the nature of forces, may be found in A. Secchi's "Die Einheit der Naturkräfte."

In the chemical union of bodies heat is almost invariably disengaged, and as it is a mode of motion, and as motion of *one* kind can only be derived from another, we must conclude that bodies acting chemically, especially the elements, do possess a peculiar kind of motion, which, in chemical union, is partially converted into heat motion (also into light and electricity). This special motion of *matter* is designated *chemical energy* or *chemical tension.* And in the chemical decomposition of a compound body into its constituents, heat is absorbed, disappears as such, and is transformed into chemical energy. Thus, for instance, in the union of 1 kilogram of hydrogen with 8 kilograms of oxygen a quantity of heat is liberated which can perform a mechanical work equal to 34.462 × 423.5

= 14,629,000 kilogrammeters. In the decomposition, on the other hand, of 9 kilos of water into hydrogen and oxygen, the same force or quantity of heat is necessary. Therefore, in the liberated hydrogen and oxygen, the same quantity of force or motion must be contained in the form of chemical energy.

Chemical energy is not only a quantitative phenomenon; it also presents qualitative differences. Although all bodies, and particularly the elements, possess it, they do not disclose it in the same way in their action upon each other. Some unite or react readily with each other; others, on the contrary, with difficulty, or not at all. The reason for this deportment is to us entirely unknown, but it is in all probability due to the different form and mode of motion of the smallest particles of matter. We designate it by the phrase *chemical affinity*, and add that bodies capable of union have affinity for each other (are related), and that by union they satisfy their *affinity*. This expression is incorrectly chosen, because, generally, the bodies least alike chemically unite with each other most readily.

CHEMICAL SYMBOLS AND FORMULAS.

For simplicity and convenience the elements are represented by the first letters of their names, derived either from the Latin or Greek. Hydrogen is represented by the letter H, from the word hydrogenium; nitrogen by N, from nitrogenium. When several elements happen to have the same letter there is added to the capital a second small letter; thus, Na represents natrium; Ni, nickel; Hg, mercury (hydrargyrum), etc. The subjoined table comprises all the elements known at present with certainty (69), together with their chemical symbols and atomic weights. The latter have been determined with more or less accuracy.

Elements.	Symbol.	Atomic Weight.	Elements.	Symbol.	Atomic Weight.
Aluminium,	Al	27.08	Molybdenum,	Mo	95.9
Antimony (Stibium),	Sb	120.3	Nitrogen,	N	14.041
Arsenic,	As	75	Nickel,	Ni	59
Barium,	Ba	137	Niobium,	Nb	94.2
Beryllium,	Be	9.1	Osmium,	Os	192
Bismuth,	Bi	208	Oxygen,	O	16
Boron,	B	11.01	Palladium,	Pd	106
Bromine,	Br	79.963	Phosphorus,	P	31.03
Cadmium,	Cd	112.1	Platinum,	Pt	194.8
Cæsium,	Cs	132.9	Potassium (Kalium),	K	39 14
Calcium,	Ca	40	Rhodium,	Rh	103
Carbon,	C	12	Rubidium,	Rb	85.4
Cerium,	Ce	140.2	Ruthenium,	Ru	101.7
Chlorine,	Cl	35.453	Samarium,	Sa	150
Chromium,	Cr	52.2	Scandium,	Sc	44.1
Cobalt,	Co	59	Sulphur,	S	32.06
Copper,	Cu	63.3	Selenium,	Se	79.1
Didymium,	Di	142.3	Silver (Argentum),	Ag	107.66
Erbium,	Er	166	Silicon,	Si	28.4
Fluorine,	Fl	19	Sodium (Natrium),	Na	23.06
Gallium,	Ga	69 9	Strontium,	Sr	87.5
Germanium,	Ge	72.3	Tantalum,	Ta	183
Gold (Aurum),	Au	197.2	Tellurium,	Te	125
Hydrogen,	H	1.003	Thallium,	Tl	204.1
Indium,	In	113.7	Thorium,	Th	232.4
Iodine,	I	126.86	Tin (Stannum),	Sn	118.1
Iridium,	Ir	193 2	Titanium,	Ti	48.1
Iron (Ferrum),	Fe	56	Tungsten (Wolfram),	W	184
Lanthanum,	La	138.5	Uranium,	Ur	239.4
Lithium,	Li	7.03	Vanadium,	Vd	51.2
Lead (Plumbum),	Pb	206.91	Ytterbium,	Yb	173.2
Magnesium,	Mg	24.38	Yttrium,	Y	88.7
Manganese,	Mn	55	Zinc,	Zn	65.5
Mercury,	Hg	200.4	Zirconium,	Zr	90.7

Holmium and thulium (the element X of Soret) might also be mentioned, although the latest researches seem to indicate that they and also erbium, didymium and samarium are not simple substances, but rather mixtures of several elements.

Compounds produced by the union of the elements are represented by placing their corresponding symbols together and designating these *chemical formulas*. Common salt, a compound of sodium and chlorine, is represented by the formula $NaCl$; mercuric oxide, a compound of mercury and oxygen, by HgO; iron sulphide by FeS; hypochlorous acid, a compound of chlorine, hydrogen and oxygen, by $ClOH$.

These chemical formulas not only express the nature of the elements, but also the relative proportions by weight, according to which they unite, compared with hydrogen as unity. Thus H represents 1 part by weight of hydrogen; Cl, 35.45 parts by weight of chlorine; Na, 23.06 parts by weight of sodium. (See table, p. 24.)

These numbers indicate the relative weights of the *atoms* constituting the elements.

If we seek to obtain a representation of the constitution of the elements and matter in general, two possibilities appear to be foremost. Either the substance continuously fills space, or it consists of very small separate particles, chemical individuals, filling space, which are termed *atoms*. The latter idea alone corresponds to the present state of physical and chemical investigation, so that the *atomic constitution of matter only has value at present.* The inductive derivation and establishment of the atomic theory will be given subsequently (see page 69); here we will only state the following propositions: Each distinct element consists of similar atoms, of like size and similar weight, while atoms of different elements possess a different weight. The absolute atomic weights are, at present, not determined with sufficient accuracy; the relative weights are referred to the hydrogen atom, which has the smallest weight, hence is made equal to 1 (H = 1). The chemical union of the atoms produces the smallest particles of compound bodies, termed *molecules*, physical individuals; these are chemically divisible. By these premises chemical formulas acquire a very precise and evident importance. The formula NaCl represents the union of 1 atom of sodium (Na) with 1 atom of chlorine, and indicates that in it 23.06 parts, by weight, of sodium are combined with 35.45 parts of chlorine. If several atoms of an element are present in a compound, this is denoted by numbers which are attached to the symbol of the atom:—

HCl	H_2O	H_3N	CH_4
Hydrochloric acid.	Water.	Ammonia.	Methane.

The formula of water (H_2O) means that its molecule consists of 2 atoms of hydrogen (2 parts by weight) and 1 atom of oxygen (O = 16 parts by weight). The formula of sulphuric acid (H_2SO_4) indicates it to be a compound consisting of 1 atom of sulphur (32.06 parts), 4 atoms of oxygen (4 × 16 = 64 parts), and 2 atoms of hydrogen (2 × 1 = 2 parts), from which the composition of the acid may be at once calculated into per cent., or into any desirable quantity by weight.

Atomic Composition.	In per cent.
Sulphur, $S = 32.06$	32.69
Oxygen, $O_4 = 64$	65.26
Hydrogen, $H_2 = 2.$	2.05
$H_2SO_4 = 98.06$	100.00

The chemical union of bodies is shown by the sign +; and the resulting products are placed to the right, following the = sign :—

$$HgS + Fe = FeS + Hg.$$

By this *equation of chemical transposition* is meant that by the union of mercury sulphide (HgS) and iron (Fe), iron sulphide (FeS) and free mercury (Hg) are formed. The equation

$$2H + O = H_2O$$

indicates that 1 molecule of water has been formed by the union of 2 atoms of hydrogen with 1 atom of oxygen.

At the same time such equations show the proportions by weight of the substances entering into and resulting from the reaction ; the weight of the acting substances is equal to that of those resulting. Therefore every chemical equation is at once an expression of the principle of the indestructibility of matter (substance). (See p. 21.)

CONDITIONS OF CHEMICAL ACTION—THERMO-CHEMICAL PHENOMENA.

The chemical changes sustained by matter, the decomposition of compounds into their constituents, or their conversion into other forms of like composition (into allotropic and isomeric modifications, see ozone and phosphorus), are only effected through external agencies, *e. g.*, by heat, electricity, or light, and also by mechanical action (compression, concussion). These agents are nothing more or less than modes of motion, and their action consists in imparting motion, which induces the chemical changes, or renders them possible. The mutual action of substances differing chemically—the formation of compound from simple bodies—occurs only when they are in intimate contact. It is only in physical changes that action at a distance is observed. The intimate contact requisite for chemical action with solids is generally not attainable by mere mechanical mixture. It is brought about by liquefying one or both of the solids, either by fusion or by solution in some solvent. In this way the physical cohesion of the molecules is diminished. The early chemists expressed these conditions by saying : *Corpora non agunt nisi fluida.* Liquid and gaseous bodies are therefore, *eo ipso*, adapted to chemical action.

Besides intimate contact, some external physical action is necessary to effect the chemical union of different bodies, or at least to induce their reaction. The agents (heat, electricity, light) employed for the decomposition of compound substances will serve this purpose. We may explain this action by saying that the atoms chemically combined with each other must often be loosened in order that they may react upon other atoms (see below).

The real cause of the chemical transposition, of the union of the atoms with each other, is ascribed usually to a special attractive force, which may be called *chemical affinity* or *attraction*. We are, however, aware that all forces are referable to modes of motion: besides, the acceptance of *chemical affinity* is very uncertain and determined with difficulty. At the ordinary temperatures hydrogen and oxygen do not react; there is apparently no affinity between them. But when they are raised to a temperature of 400°, or upon the passage of an electric spark, they unite to form water, and an explosion ensues. Again, a mixture of hydrogen and chlorine remains unaltered in the dark; their union occurs very slowly in diffused light, but very rapidly and with explosion when exposed to sunlight or under the influence of an electric spark. The affinity or tendency to combine is consequently relative; it is dependent on external conditions. Experiments have been made to ascertain how great this *affinity* or *tendency* might be; the results were not concordant. The speed of reactions was studied with this in view. For the present, at least, it is therefore better not to attempt to define or estimate the magnitude of chemical affinity.

Far better and more satisfactory results are afforded by the idea of **energy of combination**, and by the **energy-content** of the elements and compounds (p. 22). Every chemical change is invariably accompanied by a change of energy—by the disengagement or absorption of heat (electricity, etc.). The customary chemical equations, such as are employed upon p. 26, represent merely the material side of a chemical reaction, the nature and quantities by weight of the reacting and resulting substances. But when, for example, hydrogen and oxygen unite to yield water, there is an accompanying dynamical change, a definite and considerable quantity of heat is disengaged—in this instance equaling 68,000 calories (p. 66). An equation showing the union of hydrogen with oxygen to form water—an equation which would include both *weight* reactions and those of *energy*—would read as follows:—

$$2H + O = H_2O + 68{,}000 \text{ Cal.}$$

In the union of hydrogen with chlorine, forming hydrogen chloride, we have a liberation of 22,000 calories:—

$$H + Cl = HCl + 22{,}000 \text{ Cal.};$$

while the formation of hydrogen iodide from hydrogen and iodine is accompanied by an absorption of energy—an absorption of 7,000 calories:—

$$H + I = HI - 7{,}000 \text{ Cal.}$$

When we desire to decompose water into hydrogen and oxygen we must restore all the energy which has escaped (68,000 cal.). It is contained in the free elements as chemical (potential) energy. The decomposition of hydrogen iodide, on the contrary, would occur with a disengagement of energy (of 7,000 cal.).

These **alterations of energy**, consisting in the liberation and absorption of heat (electricity, etc.), constitute an important characteristic of every chemical transposition, because they afford real explanations for the course of a reaction, the mode of formation, the stability, and entire character of the resulting compounds.

Reactions are distinguished as *exothermic* and *endothermic*, depending upon whether heat (energy) is liberated or absorbed.

The union of hydrogen with oxygen to form water is an exothermic reaction (see above), and water is an *exothermic compound*. All such exothermic compounds possess less energy than their component elements; they are, consequently, more stable than these, and can only be converted into them by the addition of energy. The conditions of their formation are present in the components; for this reason they may be designated *direct* compounds. *Exothermic* reactions frequently take place immediately upon contact of the components, but usually the reaction must be induced; there must be some external impulse (by heat, electricity, etc.) given, which may be regarded as a liberation of the chemical energy, and is made manifest by the fact that the molecules of the compounds and of the elements must first be torn asunder into their component atoms. When the exothermic reaction has been induced in a part of the mixture, it will proceed farther of itself, corresponding with the quantity of heat liberated, and will advance with greater or less rapidity, and may even rise to an explosion, *e. g.*, the formation of water or hydrogen chloride from their elements (p. 67).

The *endothermic* reactions, *e.g.*, production of hydrogen iodide from iodine and hydrogen, proceed with the absorption of heat (energy). *Endothermic compounds*, *e.g.*, hydrogen iodide and nitrogen chloride, contain more energy than their components, and are, therefore, less stable than the latter, into which they pass with loss of energy. The conditions of their formation are not present in their components, but must be added from without, and on this account they may be designated as *indirect* compounds. Accordingly, *endothermic* compounds do not result by the immediate contact of their components. To effect their union there must be a constant addition of energy, otherwise the reaction will cease.

The *decomposition* of compounds into their elements or components proceeds in a manner exactly opposite to that displayed in their formation from the same components. Exothermic compounds, possessing less energy than their components, can only be separated into the latter by adding to them the entire quantity of heat which was developed in their formation. The decomposition of an exothermic compound, like that of water into hydrogen and oxygen, is, consequently, an *endothermic decomposition.* It proceeds in a manner similar to that of an endothermic compound. It requires the constant addition of energy, proceeds gradually, is *never* accompanied with explosion, and is limited by the opposite tendency of the components to unite (hydrogen and oxygen, to yield water). Compare the dissociation of water.

The endothermic compounds, on the other hand, *e. g.*, hydrogen iodide and nitrogen iodide, containing more energy than their components, separate easily and completely into the latter. An *exothermic decomposition* such as this proceeds in a manner similar to that of an exothermic compound. It only requires an external impulse when it will proceed alone, sometimes with explosion—just as hydrogen unites with oxygen and chlorine, with explosion. Endothermic compounds are, therefore, generally *explosive bodies.* Some, like chlorine oxide and nitrogen iodide, explode when touched or when warmed, others require a powerful blow. For example, nitric oxide, acetylene, and cyanogen decompose with explosion when a slight quantity of fulminating mercury is ignited in them (Berthelot).

It follows, from what has been recorded above, that exothermic reactions, liberating heat, can proceed of themselves, while the endothermic always require additional energy. We may then deduce this principle, that when several bodies react with each other *without the addition of external energy*, the reaction must proceed in the direction in which there is the greatest liberation of heat—or, that from a given system of bodies that one must result which contains the least energy, and in the formation of which the largest amount of heat has been developed. *This is the principle of the greatest development of heat.*

This principle may be considered as a special case of the principle of the mechanical theory of heat resulting from the *degradation* (dissipation), or entropy of energy, according to which every form of energy tends to pass into heat-energy. It is expressed in the principle of mechanics, that an isolated system of bodies will be in equilibrium if all the potential is converted into kinetic energy. It is due to Berthelot that this principle, in its generality, has been applied to chemical phenomena and confirmed.

This fundamental principle of the greatest heat development in no manner proves that the chemical reactions, *when in presence of* *an external energy* (heat), must invariably proceed in the direction of the heat disengagement, nor does it prove that only those bodies are formed in which there is less energy—in other words, those that have given off the greatest amount of heat. Heat separates compounds into their components, and this opposes the tendency on the part of the elementary atoms to unite. Solvents occasionally act in a manner similar to heat. At a certain temperature every compound is split into its elements (see Dissociation of Water).

At absolute zero (—273°) heat motion does not occur; at this point, then, only exothermic reactions take place. The reaction is endothermic at the temperature at which a compound is fully decomposed. As the temperatures of decomposition are mostly very high (1000–3000°), it is evident, that at ordinary temperatures most reactions belong to the exothermic class.

We must not omit the circumstance, that chemical substances do not consist of free, but of atomic-aggregations (molecules), which, in chemical changes, must first be separated into atoms, and further, that the stability of compounds (their decomposition by heat or solvents) does not always correspond to their heat of formation (p. 68). The principle of the greatest development of heat may, therefore, be formulated into the principle of maximum work-power (F. Braun). It is embraced in the following sentence: In chemical changes the *tendency* is toward the production of that body or aggregation of bodies, in whose formation there is the greatest development of heat. This principle is important in the representation and explanation of chemical changes, and will be applied in the several groups of elements which follow.

CRYSTALLOGRAPHY.

Chemistry occupies itself chiefly with the investigation of the chemical alterations of bodies. Its subject is not the latter in themselves, in their external properties, but only with reference to their material composition, and their genetic relations to other substances. The investigation of the physical properties of the non-organized bodies constitutes the province of Mineralogy, or, if the same is not limited to naturally occurring bodies, but includes also the innumerable substances which have been prepared artificially, it becomes the province of *Inorganography*. Pure chemistry considers the physical properties only as far as they serve for the external characterization and eventual recognition of the given substances and for the deduction of chemical laws. The most important physical properties,—the state of aggregation, the temperature of fusion and boiling, the specific gravity, capacity for heat, etc.—are partially treated in Physics, and in part will be considered later, in special cases.

Here, therefore, the morphological characters of the solid bodies will receive only a brief consideration.

The homogeneous solids exhibit either similar properties in all their parts, are *amorphous*, or show differences in certain definite directions, giving rise to a *crystalline* appearance. The cause of this deportment lies in the arrangement of the smallest particles of substance of the molecules, which in the first instance is irregular, hence cannot cause differences in any direction; while in the crystalline structure the molecules are regularly grouped according to directions of varying density and coherence, which find expression in the cleavage and the optical and thermal behavior of bodies. A consequence of this regular arrangement is, in the case of undisturbed formation, the external limitation of bodies by planes, edges, and angles, which represent the crystal form. The number and forms of these crystal elements are very numerous, since several thousands are known. It is, however, possible to reduce the numberless varieties to a few classes or *systems*, by comparing their modes of formation, and by referring their principal elements—the planes—to definite axes, *i. e.*, to directions or lines, which are imagined to be so placed through the middle point of the crystals that their planes lie symmetrically with reference to them. In this manner, by distinguishing the various axis-intersections, *crystallography* arrives at the following six systems of crystallization:—

1. The Regular, or Tesseral System.
2. Quadratic, or Tetragonal System.
3. Rhombic System.
4. Hexagonal, or Rhombohedral System.
5. Monoclinic System.
6. Triclinic System.

The position of any even plane in space is determined by three points of a system of coördinates, and therefore the position of a crystal face is also determined by its points of intersection with the three axes, or, by the distances from the centre of the axis at which the plane (by suitable expansion) cuts or intersects the three axes. The distances are termed the *parameters* of the plane. In the regular system all three axes are of equal length and equal value, for which reason they are designated by the same letter, a (Fig. 1). If a plane intersect all three axes at equal distances (as in the octahedron) the parameter ratio is a : a : a; if at unequal distances, the ratio is a : a : ma, or a : ma : na; in which case the parameter of the first axis is always made = 1. If a plane lie parallel to an axis intersecting it at infinity, its parameter with reference to this axis = infinity (a : a : ∞ a); if it be parallel to two axes, two parameters are = infinity (a : ∞ a : ∞ a). Hence these parameter ratios designate the position of a plane; and as all the planes in simple crystal forms are similar, these symbols represent the entire simple form, *i. e.*, the whole of all planes, which are deduced from the same parameter ratio.

In the regular system where all three axes are of equal lengths, the parameters m, n (the parameter of the first axis equaling 1) are simple rational numbers (1, $\frac{3}{2}$, 2, $\frac{5}{2}$, 3, 4, etc.). In other systems of crystallization either two or three axes are unequal, and do not stand in any rational ratio to their lengths (a : b : c), and, therefore, to the parameters of the planes (a : mb : nc); but the ratio of the parameter coefficients 1. m. n., however, in them is, as learned from experience, a simple, rational one, like that of the regular system.

According to the number of axes, five of the crystallographic systems are triaxial or *trimetric;* for practical reasons we assume the presence of four axes in the hexagonal system—*tetrametric* system. The axes of the five trimetric systems are either all at right angles to each other, and are distinguished only by varying lengths—the *orthometric* systems, the regular, the quadratic, and the rhombic; or they include, also, oblique angles—in two *clinometric* systems, the monoclinic and triclinic. In the regular system the three directions of development are at right angles and perfectly similar, for which reason the bodies belonging to it refract light simply—isometric system. Amorphous substances do the same. The remaining five systems with unlike axes, are, on the contrary, doubly refracting, and exhibit simple refraction in but *one* direction (optically *uniaxial* systems—the quadratic and hexagonal), or, in *two* directions (optically, *diaxial* systems—the rhombic, mono-, and triclinic). Bravais and Sohncke have recently suggested a geometrical derivation of the different systems of crystallization; the basis of the same is the molecular constitution of matter. The authors proceed from the possible groupings of points or molecules in space, *i. e.*, from such groupings in which about each point the arrangement of the remaining points is the same. In this way it is possible to embrace the point positions which can occur in space into seven groups, corresponding to the seven crystallographic systems. The rhombohedral forms, which crystallography views as the hemihedral of the hexagonal, then appear as an independent system.

1. **Regular System.**—The crystals of this system are similarly developed in three directions, and therefore have three similar axes, a, of the same length, which intersect each other at right angles (Fig. 1). If we imagine the faces of the crystal arranged in such manner that they intersect the three axes at similar or dissimilar distances, we have the following seven simple forms for the various possible parameter ratios (page 31):

1. The *octahedron* (Fig. 2), with the parameter ratio a : a : a; for which the abbreviated symbol O may be written. 2. The *cube*, or hexahedron (Fig. 3), with the symbol a : ∞ a : ∞ a or briefly ∞ O ∞. 3. The rhombic dodecahedron, twelve sides, a : a : ∞ a or ∞ O (Fig. 4). 4. The trigonal tris-octahedron (Fig. 5), a : a :

ma or mO; there are several of these, as m can equal $\frac{3}{2}$, 2, or 3. 5. The trapezohedron (Fig. 6), a : ma : ma or mOm, in which m = 2 (in garnet) or m = 3 (in ammonium chloride). 6. The tetrahexahedron (Fig. 7), a : ma : ∞ a or mO ∞, in which m = $\frac{3}{2}$, 2, or 3. 7. The hexoctahedron (Fig. 8), a : ma : na or mOn, where, *e. g.*, in fluorite, m = 2 and n = 3.

FIG. 1.

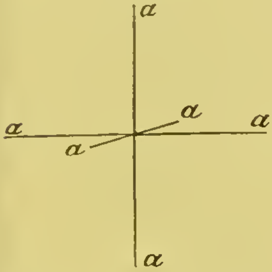


FIG. 2.

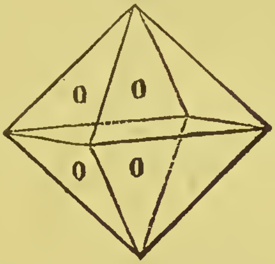


FIG. 3.

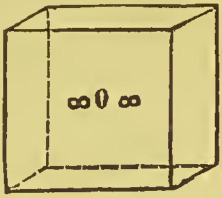


FIG. 4.

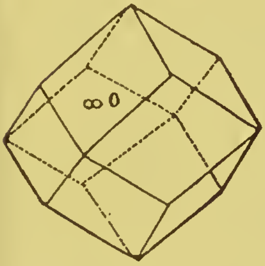


FIG. 5.

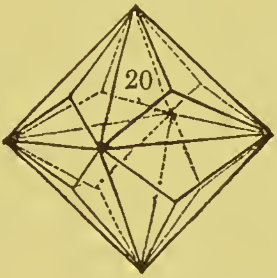


FIG. 6.

These seven simple forms may appear combined on one crystal, and we thus obtain *crystal combinations*. For example, Fig. 9 represents a combination of octahedron and cube (on alum); Fig. 10, a combination of octahedron, cube, and dodecahedron (galenite).

FIG. 7.

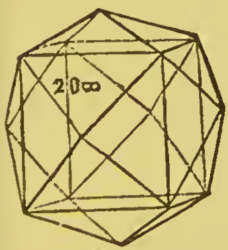


FIG. 8.

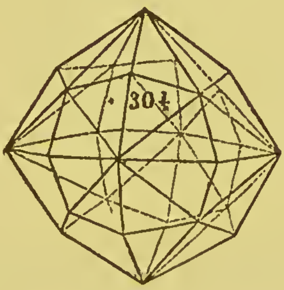
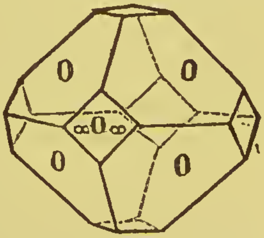


FIG. 9.



In addition to these simple forms, appearing with their full number of planes, hence termed *holohedral*, others are found having only the half or fourth of the possible faces, *hemihedral* or

FIG. 10.

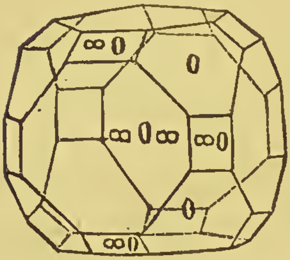


FIG. 11.

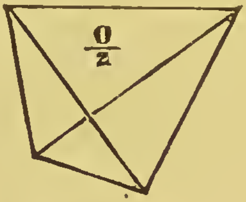
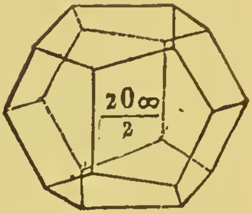
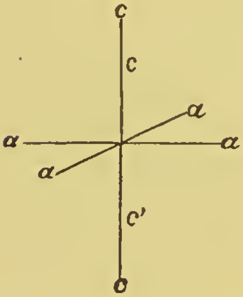


FIG. 12.



tetartohedral forms. We may suppose them produced by the enlargement of the symmetrically distributed half number of faces of the holohedral form, and therefore they are marked with the corresponding holohedral symbol divided by 2. Such hemihedral forms are: The tetrahedron $\pm\frac{O}{2}$ (Fig. 11), resulting from the octahedron, and the pentagonal dodecahedron $\frac{mO\infty}{2}$ (Fig. 12) derived from the tetrahexahedron.

FIG. 13.



2. **Quadratic System.**—Crystals of this system are developed at right angles in three directions, of which two are alike, the third unlike the others. Therefore, they possess two equal secondary axes, a, and an unequal, longer or shorter, principal axis, c (Fig. 13). The axis ratio, therefore, is a : a : c; the ratio of a : c is definite but not rational for every body of the system (see page 31), *e.g.*, for tin 1 : 0.3857. The principal (ground) form* of this system is the *quadratic pyramid* a : a : c, with the symbol P, an *obtuse pyramid* (Fig. 14) if c be smaller, or an *acute pyramid* if c is greater than a. From these pyramids of the *first order*, in which the axes pass through the angles, we distinguish pyramids of the *second order*, in which the two secondary axes pass through the middle of the edges. The planes of the latter are parallel to one secondary axis, therefore its symbol is a : ∞a : c, or P∞. Fig. 15 represents a combination of a pyramid of the first and second orders.

In addition to the above pyramids, others may occur upon the same crystal, which intersect the principal axis at the distance mc. In this case m is also a simple rational number, *e.g.*, 3, 2, ½, ⅓, etc. The symbol of such secondary

---

* The principal (ground) form is that to which the remaining forms of the same mineral may be most readily referred.

pyramids of first order, is a : a : mc = mP : that of the second order, a : ∞ a : mc = mP∞. The coefficient of the principal axis is always written before P.

If the pyramid planes intersect the principal axis at infinity, the *quadratic prism* results, and, indeed, either a prism of the first order, with the symbol a : a : ∞ c = P∞ ; or a prism of second order, a : ∞ a : ∞ c = ∞ P∞. Fig. 16 represents a combination of the quadratic prism with the quadratic pyramid, as seen on zircon and potassium phosphate. With the parameter ratio of the planes, a : ma : nc, we get the ditetragonal pyramid nPm. Its corresponding ditetragonal prism has the symbol a : ma : ∞ c = ∞ Pm.

FIG. 14.

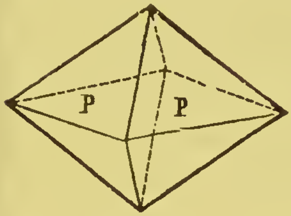


FIG. 15.

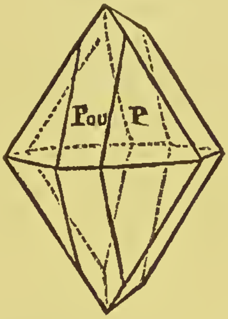
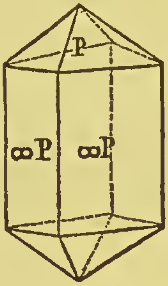


FIG. 16.



Different hemihedral forms are possible in this system, of which may be mentioned the *tetragonal sphenoid* $\pm \frac{P}{2}$, corresponding to the tetrahedron. Chalcopyrite, tin, potassium phosphate, etc., crystallize in this system.

FIG. 17.

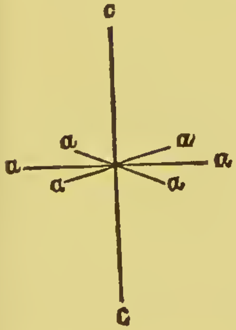


FIG. 18.

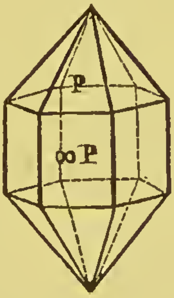
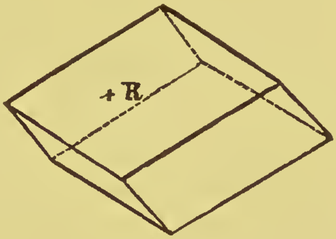


FIG. 19.



3. **Hexagonal System.**—The forms of this system, like those of the preceding, exhibit *one* peculiarly striking direction of development, and hence this is chosen as the direction of the principal axis c. They are distinguished from the four-sided forms of the quadratic system by their sixfold symmetry, which finds expres-

sion in their equal secondary axes (Fig. 17), intersecting each other at 60°. The principal axis is at right angles to these. The axis ratio is $a : a (: a) c$, and the ratio of $a : c$ for every substance is definite, but not rational; *e.g.*, in quartz, 1 : 1.100; calcite, 1 : 0.8543, etc.

The fundamental (ground) form of the system is the hexagonal pyramid $a : a : (\infty a) : c = P$, from which is derived the hexagonal prism $a : a : (\infty a) : \infty c = \infty P$; and, indeed, as in the quadratic system, there are pyramids and prisms of first and second order—the latter with the symbol $a : 2a : (2a) : c = P2$, and $a : 2a : (2a) : \infty c = \infty P2$. Further, other pyramids can occur, intersecting the principal axis, at the distance mc; their symbol is mP and $mP2$. Fig. 18 represents the combination of pyramids and prisms found on apatite. With the common parameter ratio $a : na : (ra) : mc$ (in which the parameter of the third secondary axis, ra, is always given as in all other hexagonal forms, by the parameters of the first two secondary axes), result the dihexagonal pyramid, mPn, and the dihexagonal prism, ∞Pn.

FIG. 20.

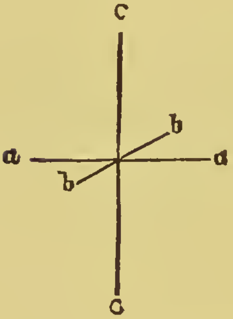


FIG. 21.

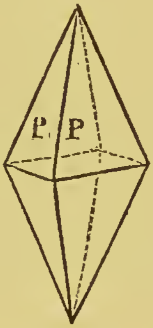
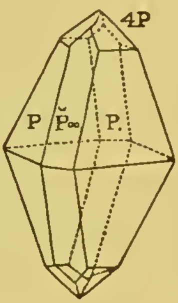


FIG. 22.



The rhombohedra $\pm\frac{mP}{2} = \pm mR$ (Fig. 19) are the hemihedral forms of the pyramids mP, produced by the growth of the alternate faces. Another important hemihedral form is the *scalenohedron* $\pm\frac{mPn}{2}$ derived from the dihexagonal pyramid. It is a remarkable fact that the hemihedral forms of the hexagonal system occur much more frequently in nature in numberless combinations (especially in calcite), and they are, therefore, sometimes treated as a separate system.

4. **Rhombic System.**—Three axes of unequal length, a. b. c., at right angles to each other. Any one, as c, is chosen as principal axis, and of the secondary axes, the shorter a is designated as the brachydiagonal, the longer b as macrodiagonal (Fig. 20). The

axis ratio a : b : c is definite for every substance, *e. g.*, for sulphur, 0.811 : 1 : .0899.

The principal forms of the system are the rhombic pyramid, a : b : c = P (Fig. 21), the rhombic prism a : b : ∞ c = ∞ P, and the *domes*—brachydiagonal ∞ a : b : c = $\breve{P}$ ∞ and the macrodiagonal a : ∞ b : c = $\bar{P}$ ∞, consisting of two pairs of planes. Fig. 22 shows a combination of two pyramids with the brachydiagonal dome. Sulphur (native and that crystallized from carbon disulphide), potassium nitrate, aragonite and barite belong to this system.

5. Monoclinic System.—Three unequal axes, two at right angles to each other, the third, however, at right angles with one and oblique to the other (Fig. 23); a is at right angles to b and to c, but c is oblique to b at the angle β. The crystals of this system are mostly developed according to an axis oblique to another (c to b), and hence one of these is chosen as principal axis c. Of the two secondaries, b is called the clinodiagonal, and a the orthodiagonal. The axis ratio is always definite for every substance; *e. g.*, for ferrous sulphate 1.1704 : 1 : 1.5312 with the angle $\beta = 76° 33'$. The monoclinic pyramid is the principal form a : b : c = P, consisting of two hemipyramids, + P and — P (Fig. 24). It corresponds to the monoclinic prism ∞ P. Sulphur (fused), soda, borax, di-sodium phosphate ($HNa_2PO_4 + 12H_2O$), Glauber's salt, and orthoclase, crystallize in this system.

FIG. 23.

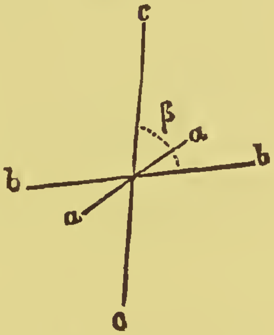


FIG. 24.

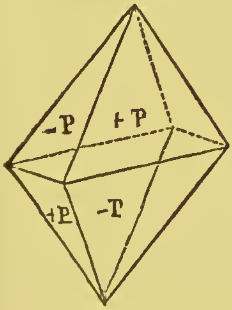


FIG. 25.

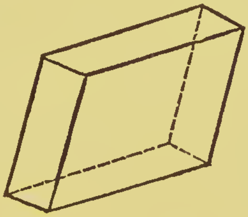
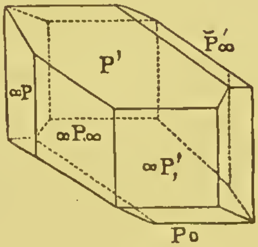


FIG. 26.



6. Triclinic System.—Three unequal axes all oblique to each other. The axis ratio a : b: c, and the three angles are definite for each substance. The forms of this system are very complicated, since the triclinic pyramids P must be considered as consisting of four quarter pyramids, and the triclinic prism ∞ P (Fig. 25), of two hemiprisms. Potassium dichromate, albite, boracic acid, and copper sulphate crystallize in this system. Fig. 26 represents one of the common forms of the latter.

Crystals found in nature have grown, and therefore rarely occur so regularly developed as represented in the preceding drawings. They are usually developed more or less in the direction of single axes, and on that account the faces of the same form are unlike, and the entire crystal appears distorted. But the position of the planes with reference to the axes and the angles which they form with each other, always remain unchanged. Therefore the measurement of the angle of the planes by means of the goniometer serves as the only accurate means of determining complicated crystalline forms; we calculate the axis ratio from the angles.

Substances crystallizing in two or three different systems are said to be *dimorphous*, or *trimorphous* (see sulphur). Different substances crystallizing in the same or very similar forms are termed *isomorphous* (compare Isomorphism).

SPECIAL PART.

CLASSIFICATION OF THE ELEMENTS.

Ordinarily we are accustomed to divide the elements into two groups: metals and metalloids (see p. 20). The former possess metallic appearance, are good conductors of heat and electricity; the latter, or non-metals, do not have these properties, or at least in less degree. In chemical respects the metalloids have the tendency to combine with hydrogen, forming volatile, generally gaseous, compounds; their oxygen derivatives form *acids* with water. The metals, on the contrary, rarely unite with hydrogen, and their oxygen derivatives yield chiefly the so-called *bases* with water. Further, the binary compounds of metals with the metalloids are so decomposed by the electric current that the metal separates at the electro-negative, and the metalloid at the electro-positive pole. From this we observe the metals are more electro-positive—more basic; the metalloids more electro-negative—of an acid-forming nature. A sharp line of difference between metals and metalloids does not exist. There are elements which in their external appearance resemble metals, while in a chemical respect they deport themselves throughout as metalloids, and *vice versa*. Thus hydrogen, a gaseous element, is like the metals in its entire chemical character, while metallic antimony arranges itself with the metalloids.

It is therefore advisable to divide the elements into separate natural groups, based upon their chemical analogies. The best and only correct classification of all the elements depends on the law of *periodicity*, according to which the properties of the elements and of their compounds present themselves as a *periodic function* of the *atomic weights*. Later we shall treat of the periodic system more at length; it forms the basis of this text-book, and in accordance with this doctrine we consider the elements in single natural groups of similar chemical deportment. The first of these groups, comprising almost all the so-called non-metals and some metals, are the following:—

Fluorine	Oxygen	Nitrogen	Carbon	Boron
Chlorine	Sulphur	Phosphorus	Silicon	
Bromine	Selenium	Arsenic	Germanium	
Iodine	Tellurium	Antimony	Tin	
		Bismuth		

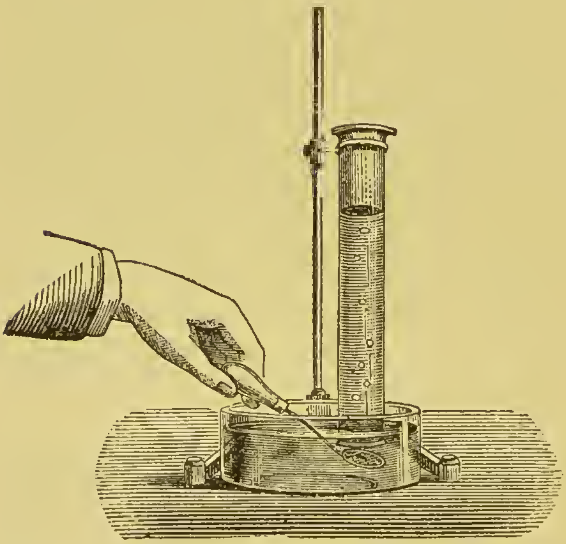
Hydrogen does not belong to any of these groups; uniting the metallic and non-metallic characters in itself, it represents, as it were, the type of all elements, and therefore it will receive first attention. Boron occupies an isolated position. It has been classed with the non-metals, but differs somewhat from them in chemical deportment. It forms the transition to the metallic elements, beryllium and aluminium.

HYDROGEN.

$H = 1(1.003)\ H_2 = 2.$

Hydrogen (Hydrogenium), a gaseous body, is rarely found in a free condition upon the earth's surface, as it combines readily with the oxygen of the air. It is present in considerable quantity in the photosphere of the sun and fixed stars. In combination, it is found chiefly as water, and in substances of vegetable and animal origin. Paracelsus first discovered this element in the sixteenth century, and called it inflammable air. In 1781 Watts and Cavendish showed that water resulted from the combustion of hydrogen in the air. In 1783 Lavoisier proved that hydrogen was a constituent of water—a chemical compound of the elements hydrogen and oxygen.

Fig. 27.



Preparation.—It may be readily obtained from water, a compound of hydrogen and oxygen. The decomposition of the same by the removal of oxygen can be effected by some metals, like Na and K, at the ordinary temperature. Both metals act very energetically upon it, liberating gaseous hydrogen. To perform the experiment, take a piece of sodium, roll it up in a piece of wire gauze, and shove it, with nippers, under the mouth of a glass cylinder filled with and inverted over water (Fig. 27). Bubbles of hydrogen are at once disengaged, displace the water and collect in the upper part of the cylinder. The reaction occurring between the sodium and water is expressed by the following chemical equation :—

$$\underset{\text{Water.}}{H_2O} + \underset{\text{Sodium.}}{Na} = NaOH + \underset{\text{Hydrogen.}}{H}$$

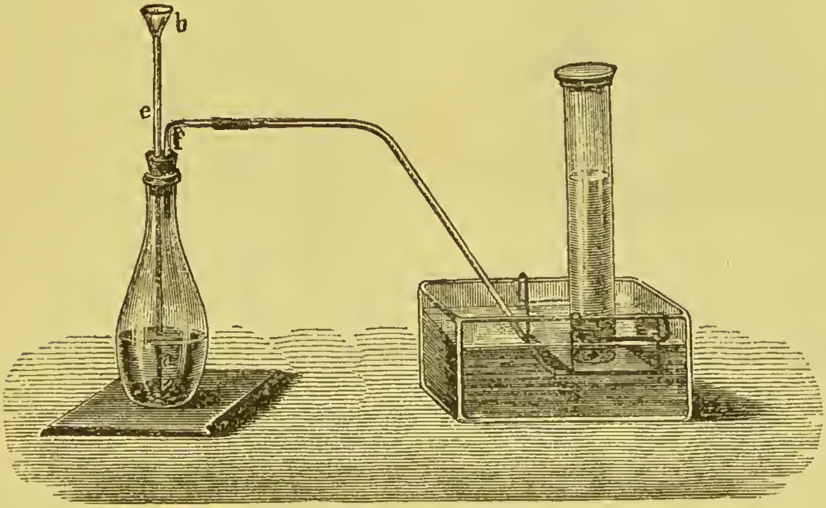
The compound NaOH, known as sodium hydroxide, remains dissolved in the excess of water.

Other metals decompose water in a similar manner, at an elevated temperature. To effect this with iron allow steam to pass through a tube filled with iron filings, exposed to a red heat in a combustion furnace. The iron withdraws oxygen from the water, combining with it, while the hydrogen set free is collected.

For laboratory purposes, hydrogen is prepared by the action of zinc upon hydrochloric or sulphuric acid. The reaction with the latter acid is as follows :—

$$Zn + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Zinc sulphate.}}{ZnSO_4} + 2H.$$

FIG. 28.



Place granulated zinc (obtained by dropping molten zinc into water) in a double-necked flask (Fig. 28), and introduce sulphuric acid (diluted with about 3 vols. of H_2O) through the funnel tube, *b*. The liberation of gas begins immediately, and the hydrogen, escaping through the exit tube, *f*, is collected as previously described.

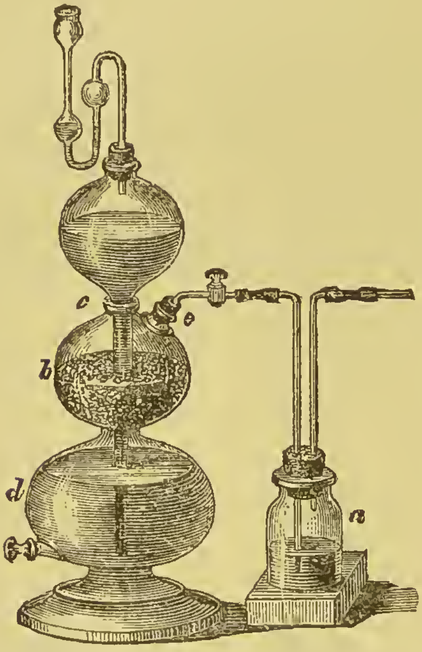
The hydrogen thus formed has a faint odor due to a slight admixture of foreign substances. It is therefore conducted through a solution of potassium permanganate to purify it.

Pure hydrogen may be obtained by heating potassium formate with potassium hydroxide: $CHO_2K + KOH = K_2CO_3 + 2H$; or by heating a mixture of zinc dust and calcium hydroxide (slaked lime) in a combustion tube: $Zn + CaO_2H_2 = ZnO + CaO + H_2$.

Purifying and Drying of Gases.—To free gases of the substances mechanically carried along during their disengagement, it is best to conduct them through variously constructed wash-bottles, filled with water or liquids, that will absorb the impurities. Ordinarily the so-called Woulff's bottles are employed (compare Figs. 36 and 42). The open tube, placed in the middle tubulure, is called the safety tube. It serves to equalize the inner pressure with that of the external atmosphere.

Gases liberated from an aqueous liquid are always moist, as they contain aqueous vapor. To remove this conduct them through vessels or tubes filled with hygroscopic substances (see Fig. 34). Calcium chloride, burnt lime, sulphuric acid, etc., are used for this purpose.

FIG. 29.



Apparatus for the Generation and Collection of Gases.—In the apparatus pictured in Fig. 28, the liberation of hydrogen continues uninterruptedly as long as zinc and sulphuric acid are present. To control the generation of the gas, we have recourse to different forms of apparatus. One of the most practicable of these is that of Kipp. It consists of two glass spheres, *d* and *b*, Fig. 29, in the upper opening of which there is a third sphere, *c*, fitting air-tight and provided with an elongated tube. It serves as a funnel. Granulated zinc is placed in the middle sphere through the tubulure *e*, and dilute sulphuric acid is poured into the spherical funnel, which first fills *d*, then ascends to *b*, where it comes in contact with the metal; at once the evolution of hydrogen commences and the gas escapes through *e*. Upon closing the stop-cock of the tube fixed in *e*, the hydrogen that is set free presses the sulphuric acid out of *b*, and consequently the liberation of the gas ceases. On again opening the cock, the acid rises in *b* to the zinc, and the evolution of gas commences anew. The vessel *a* contains water to wash the escaping hydrogen.

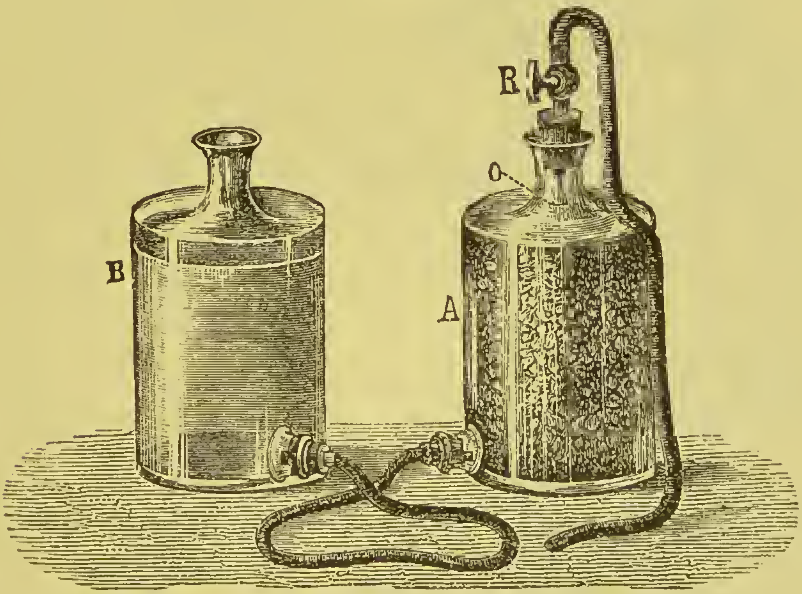
The somewhat complicated Kipp apparatus may be advantageously replaced by the following simple contrivance (Fig. 30). Two bottles provided with openings near their bottom, in which are glass tubes, are connected by a rubber tube. The bottle *A* is filled with granulated zinc, and *B* with dilute sulphuric acid. The cock *R* closes *A*. When this is opened the sulphuric acid flows from *B* to *A*, to the zinc, and the evolution of gas commences. On closing the stop-cock the hydrogen presses the acid back, from *A* to *B*; the evolution of gas ceases. By elevating and sinking the flasks the regulation can be hastened.

Gasometers of various construction serve to collect and preserve gases. In Fig. 31 we have the ordinary gasometer of Pepys. It is constructed from sheet copper or zinc, and consists of two cylindrical vessels, the lower one closed, the upper open, communicating with each other by the two tubes *a* and *b*. The tubes *c* and *c* are only supports. To collect gases in this apparatus it must first be filled with water. To this end, pour water into the upper cylinder, and open *a* and *e*; the water then flows through *a*, nearly reaching the bottom of the lower cylinder, while the air escapes through *e*. The side glass tube *f*, allows the operator to observe the height of the water-level. When the lower cylinder is filled with water close *a* and *e* (the last traces of air can be removed by opening *b*). To fill the gasometer with gas, remove the cover of the side tubulure *d*, and introduce the tube from which the gas is escaping. The latter rushes up into the cylinder, while the water flows out the tubulure. When the water is displaced by the gas, close *d*, after filling the upper cylinder, and then, if desired, open *a*, and the gas can be set free, either by *c* or *b*.

In addition to the gasometer described, various other forms are employed; gas-bags are very well adapted for preserving gases.

Physical Properties.—Hydrogen is a colorless, odorless, and tasteless gas. It has a metallic character, and in accord with this it conducts heat and electricity better than all other gases. This may be proved by the following experiment: A current of electricity is sent through a thin platinum spiral, and while the latter remains in the air or some other gas, it will glow, but in an atmosphere of hydrogen the spiral will not become luminous, or at once cease glowing.

FIG. 30.

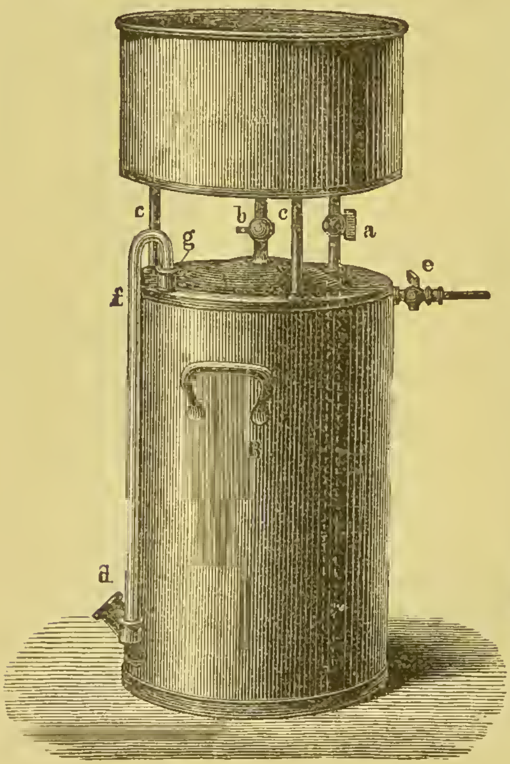


Of all gases hydrogen is the most difficult to liquefy, because its critical temperature is the lowest (about —180°); it must, therefore, be exposed to the most intense cold (p. 48). Pictet subjected it to a pressure of 650 atmospheres and a temperature of —150°. When the cock of the compression apparatus was opened (p. 48) the hydrogen escaped as a steel-blue liquid, which evaporated rapidly.

Cailletet and Wroblewsky, employing the compression method of Cailletet, which is that of the rapid expansion of a strongly compressed gas (p. 48), only succeeded in obtaining the hydrogen in the form of a gray mist. Olczewsky, however, maintains that compressed hydrogen, in a mixture with compressed oxygen, is a colorless liquid.

Like all gases, coercible with difficulty, hydrogen is but slightly soluble in water, 100 volumes dissolving 1.9 volumes H at 0°—20° C. The coefficient of absorption of hydrogen by water is therefore 0.0193. It is the lightest of all gases. A cubic decimetre (= 1 litre) of hydrogen, according to Regnault's determinations, weighs 0.089567 grams at 0° and an atmospheric pressure of 760 millimeters (at Paris), while a litre of air, under similar conditions, weighs 1.29318 grams.

Fig. 31.



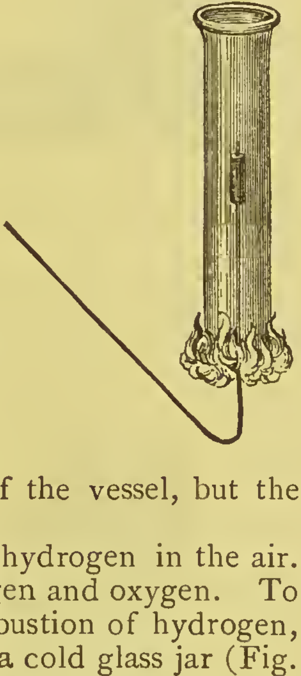
Hydrogen is, therefore, 14.43 times lighter than air. Its specific gravity, or, more correctly, its gas density compared with air as unity, is $\frac{1}{14.43} = 0.06928$. Hydrogen has been selected as unit in the determination of the specific gravity of gases, because it possesses the smallest density, and because it is well adapted thereto for chemical reasons. If the specific gravity of gases compared with H = 1 be represented by A, and the specific gravity compared with air = 1 by D, then $A = D \times 14.43$ and $D = \frac{A}{14.43}$.

Fig. 32.

That hydrogen is lighter than air is shown by a balloon of collodion or gum filled with the former rising in the latter; this can also be seen in soap bubbles filled with hydrogen. In consequence of its levity, hydrogen may be collected in inverted vessels (opening turned down) by replacing the air, and can also be poured from one cylinder into another, as is represented in Fig. 32. The hydrogen flows from the inclined cylinder into the one held vertically and filled with air, which it expels. Such a separation of gases, based on their varying specific gravity, is only temporary, as they soon mingle with each other by diffusion. By virtue of its levity and mobility, which the kinetic gas-theory attributes to the great velocity of the gas particles, hydrogen penetrates porous bodies with ease, and diffuses through both animal and vegetable membranes, as well as through gutta-percha. Consult air, upon diffusion of gases. Metals, *e. g.*, iron, platinum, palladium, permit a free passage to hydrogen, when they are raised to a red heat. They are impenetrable to other gases. This behavior is in part probably dependent upon the chemical attraction of these metals for hydrogen.

Chemical Properties.—Hydrogen is characterized by its ability to burn in the air, when it combines with the oxygen of the latter and forms water; hence its name hydrogenium (from ὕδωρ, water, and γεννάω, I produce). Its flame is faint blue, and almost non-luminous, but possesses a very high temperature. When a mixture of hydrogen and air is ignited a violent explosion ensues; therefore, before bringing a light in the vicinity of hydrogen disengaged in a vessel filled with air, allow the latter to fully escape, otherwise the vessel will be shattered to pieces by the explosion.

FIG. 33.

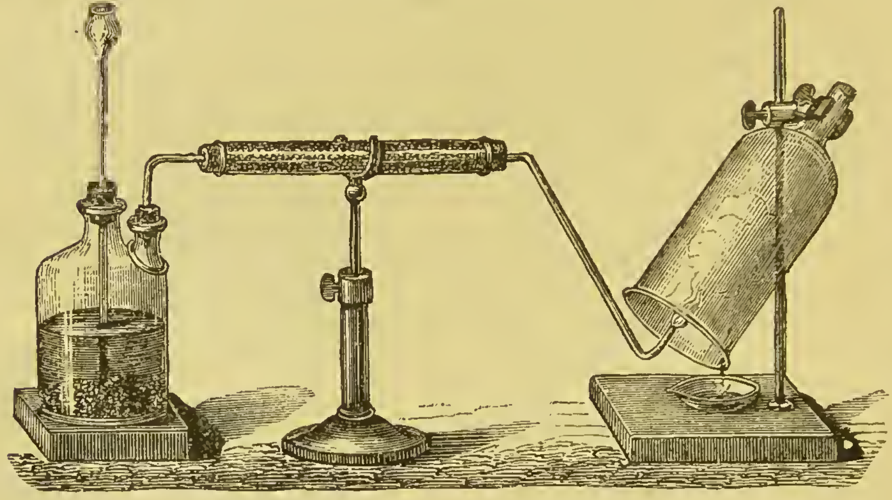


As hydrogen itself is inflammable, it cannot sustain the combustion of other bodies which will burn in the air. If a burning candle be introduced into an inverted cylinder containing an atmosphere of the gas (Fig. 33) the latter will ignite at the mouth of the vessel, but the candle will be extinguished.

Water is the product of the combustion of hydrogen in the air. It is a chemical compound containing hydrogen and oxygen. To render the formation of it visible, by the combustion of hydrogen, the flame of the latter is made to burn under a cold glass jar (Fig. 34). The sides of the latter are soon covered with moisture, which collects in drops of water. To avoid any deception the hydrogen is first conducted through sulphuric acid or a tube filled with calcium chloride, to absorb all moisture.

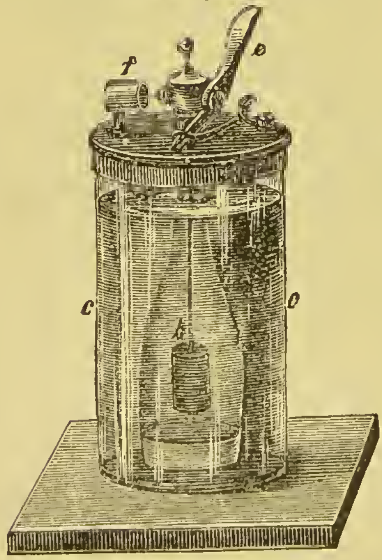
The union of hydrogen with oxygen to form water occurs only at high temperatures: at a red heat, in contact with a flame, or by the passage of an electric spark through the mixture. The combination can be effected at ordinary temperatures with the aid of platinum sponge; the latter consists of finely divided metal, obtained by the ignition of ammonio-platinum chloride (see Platinum). If a stream of hydrogen be directed upon a piece of freshly ignited platinum sponge, the gas will at once ignite. This is due to the power of the metal to condense hydrogen and oxygen upon its surface, and thereby increase their ability to unite.

Fig. 34.



Upon this behavior depends the action of the so-called *Dœbereiner Lamp* (Fig. 35). This is a continuous hydrogen generator. The outer glass cylinder *c*, is filled with dilute sulphuric acid, into which projects the pear-shaped vessel *b*. This is open below and above, and is provided with a stop-cock, *e*, affording communication with the air; in it a piece of zinc is suspended by a wire. On opening the stop-cock the sulphuric acid presses from the outer cylinder *a* into *b* and meets the zinc—when the liberation of hydrogen begins. The stop-cock directs the gas upon the support, *f*, in which is fixed some platinum sponge that effects the ignition. Upon again closing *e* the gas causes the acid to recede from the inner vessel, the zinc is freed of acid, and the hydrogen evolution ceases.

Fig. 35.



The absorption of hydrogen by the metal palladium is very characteristic. As already known, water is so decomposed by the electric current that hydrogen separates at the electro-negative pole and oxygen at the electro-positive. Now, if a piece of palladium, in sheet or wire form, be attached to the electro-negative pole, the disengagement of hydrogen does not occur, because it is absorbed by the palladium, in a quantity over nine hundred times the volume of the latter. Palladium also absorbs hydrogen when it is heated to 100°. The palladium expands, becomes lighter in weight, but retains its metallic appearance. Its tenacity and power of conducting heat and electricity are but little impaired. The compound of palladium and hydrogen, Pd_2H, therefore, conducts itself like an alloy of two metals. From the specific gravity of the compound (according to Graham), the specific gravity of the condensed hydrogen is really found to be 0.62 (water $= 1$), and is, therefore, somewhat heavier than the metal lithium. The metals potassium and sodium absorb hydrogen when heated from 200° to 400°, forming alloys (Na_2H and K_2H) in which the density of hydrogen is again equal to 0.62. These facts prove the metallic character of hydrogen, which is also indicated by its ability to conduct heat and electricity. According to Pictet liquid hydrogen has a metallic appearance (p. 43). Later, we will observe that this element displays the character of a metal in its entire chemical deportment, and that it must be regarded as a gaseous metal at ordinary temperatures.

CONDENSATION OF GASES.

CRITICAL CONDITION.

Until recently hydrogen and several other gases (oxygen, nitrogen, carbonous oxide, methane, nitric oxide), were considered as non-condensable—permanent gases, inasmuch as all attempts to liquefy the same were failures, notwithstanding Natterer (1852) had employed a pressure of 3,600 atmospheres for this purpose. These negative results find their explanation in a general property of gases, first recognized by Andrews (1871), and called by him the *critical condition* of matter. There is a temperature common to all gases, above which they cannot be condensed—this is the *critical temperature*. It was first observed with carbon dioxide (see this). Again, Caignard de la Tour (1822) showed that all liquids when heated above a certain temperature (the same critical temperature), would be transformed into gases (absolute boiling point of Mendelejeff), although they were subjected to intense pressure (in closed tubes). The pressure exerted by the gas at the critical temperature (at which it would immediately condense upon lowering the temperature) is called the *critical pressure*; the volume filled by the substance at this time is the *critical volume*.

An explanation of the existence of the critical condition is afforded by the consideration, that at the critical temperature and pressure the volume of the gas (or saturated vapor) is equal to the volume of an equal quantity, by weight, of the liquid—there exists no longer a difference between the gaseous and liquid condition.

That the gases may be liquefied, we need not only a pressure, but also a definite temperature, and this must be lower than the *critical*. By this means Cailletet and Pictet (1879) succeeded in condensing nearly all the permanent gases. Pictet pursued the method of Faraday, who had condensed various gases in sealed tubes (see condensation of chlorine (p. 51). The gases were generated in a powerful, iron retort (oxygen from potassium chlorate; hydrogen from sodium formate) by the application of heat. They were then allowed to be compressed under their own pressure in a copper tube attached to the retort. Solid carbon dioxide surrounded the tube, and by its evaporation under the air pump its temperature was reduced to —140° C. On opening the cock of the copper tube, the liquefied gas escaped in a stream which rapidly evaporated. Cailletet employed a capillary glass tube, provided with a reservoir, and a pressure pump. The strongly compressed gas was cooled by opening a cock and permitting it to expand suddenly. In its expansion and in overcoming the external pressure it performs work and there follows an absorption of an appreciable quantity of heat, which is taken from the gas. This causes a partial liquefaction of the gas in the form of a dense cloud, or in small drops.

It is better to liquefy the gas compressed in a glass tube by external cooling. This may be effected by vaporizing solid CO_2, or liquid ethylene under an air pump, when the temperature of the latter will fall to —150° at a pressure of 10 mm. In this way Wroblewsky and Olczewsky, and also J. Dewar (1883) succeeded in obtaining oxygen, carbon monoxide and nitrogen in the liquid form (static liquids). Lower temperatures, necessary for the liquefaction of hydrogen gas, may be obtained by the vaporization of liquid oxygen or nitrogen. The first of these boils under a pressure of 9 mm. at —211.4°, the second at —255° with a pressure of 4 mm. Temperatures lower than these can only be reached by the evaporation of liquid hydrogen.

The critical temperatures (T) and critical pressures in atmospheres (P) of the gases condensed with difficulty are as follows:—

	T	P
Carbon dioxide, CO_2	+ 31°	73.6 atm.
Ethylene, C_2H_4	+ 9.2°	58 “
Nitric Oxide, NO.	— 93°	71 “
Marsh gas, CH_4	— 82°	55 “
Oxygen, O_2	— 113°	50 “
Carbon Monoxide, CO . . .	— 141°	35 “
Nitrogen, N_2	— 146°	33 “
Hydrogen, H_2	— 180° (about)	99 “ (calculated).

The lowest temperatures are ascertained by means of a hydrogen thermometer or a thermo-electric element composed of copper and German silver.

The critical temperature, pressure and volume can be determined not only experimentally, but may also be deduced from the variations of the gases from the laws of Boyle and Gay-Lussac, by the following equation of van der Waals :—

$$\left(p + \frac{a}{v^2}\right) (v - b) = (1 + a) (1 + b) (1 + at).$$

From this formula the values of the critical volume (V), of the critical pressure (P), and the critical temperature are found to be

$$V = 3b \qquad P = \frac{a}{27b^2} \qquad 1 + \alpha T = \frac{8}{27} \cdot \frac{b}{a} \text{ (approximately)},$$

in which a and b represent the constants of the above equation.

HALOGEN GROUP.

To this group belong chlorine, bromine, iodine, and fluorine. These elements show a similar chemical deportment. They are termed *halogens* or *salt producers*, because by their direct union with the metals salt-like derivatives result.

1. CHLORINE.

$Cl = 35.453$. $Cl_2 = 70.906$.

It does not occur free in nature, as it is endowed with strong affinity for the majority of the elements. Its most important derivative is sodium chloride, or rock salt, which is composed of chlorine and sodium. The Swedish chemist, Scheele, discovered chlorine in 1774. Its elementary character was first established by Gay-Lussac and Thénard in France (1809), and by Davy in England (1810).

Preparation.—To obtain free chlorine, heat a mixture of black oxide of manganese (MnO_2) and hydrochloric acid in a flask (Fig. 36), provided with a so-called Welter's safety-tube to equalize the gas pressure. The escaping gaseous chlorine is washed and freed from acid that is carried along mechanically by passing it through water in a three-necked Woulff's bottle, and then collecting it over water. The reaction which occurs above is indicated in the following equation :—

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.$$

The manganous chloride formed dissolves in the water.

The evolution of the chlorine proceeds more regularly if a mixture of manganese oxide (5 parts), sodium chloride (4 parts) and sulphuric acid (12 parts diluted with 6 of water) is employed :—

$$\underset{\text{Manganese dioxide.}}{MnO_2} + \underset{\text{Sodium chloride.}}{2NaCl} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = MnSO_4 + Na_2SO_4 + Cl_2 + 2H_2O.$$

This reaction comprises two phases: First, the sodium chloride (NaCl) is decomposed by the sulphuric acid, yielding sodium sulphate and hydrochloric acid:—

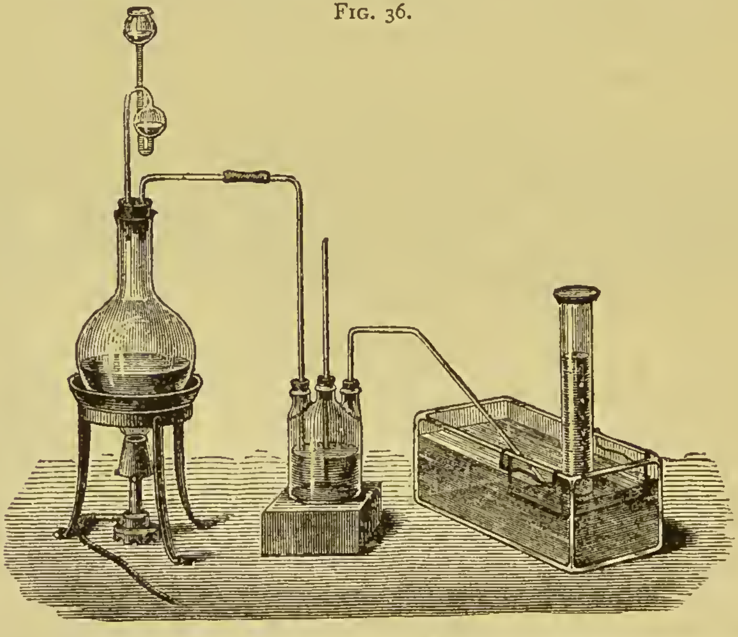
$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

The latter acid then acts, together with a new portion of sulphuric acid, upon the manganese dioxide:—

$$MnO_2 + H_2SO_4 + 2HCl = MnSO_4 + 2H_2O + Cl_2.$$

The second method is more advantageous for laboratory purposes; the first, however, is preferred in practice, as it is cheaper.

FIG. 36.



The resulting manganous chloride ($MnCl_2$) is converted by the *Process of Weldon* into manganese peroxide (see this). Technically, chlorine is also obtained by the *Process of Deacon*, by conducting HCl mixed with air over strongly ignited porous substances (bricks) saturated with metallic salts (copper sulphate).

An excellent laboratory method for the preparation of chlorine consists in allowing dilute hydrochloric acid to act upon bleaching lime (see this). The latter is previously mixed with burnt gypsum (¼ pt.), and a little water added, when the mass can be formed into cubes or stout sticks which are introduced into a Kipp generator (p. 42) (Winkler, *Berichte*, 20, 184).

As chlorine gas dissolves readily in cold water it is advisable to collect it over warm. It cannot be collected over mercury, as it readily combines with the latter. When perfectly dry chlorine is sought, conduct the liberated gas through Woulff's bottles containing sulphuric acid, to absorb the moisture, then collect in an empty upright flask (compare Fig. 44, p. 63). As chlorine is so much heavier than air it will displace the latter.

Physical Properties.—Chlorine is a yellowish-green gas (hence its name from χλωρὸς), with a penetrating, suffocating odor. Its specific gravity compared with hydrogen (1) is 35·45; with air (= 1) it is $\frac{35.453}{14.43}$ = 2.45. At 15° C., and a pressure of 4 atmospheres (at —40° C., under the ordinary pressure) it condenses to a yellow liquid, boiling at —33·5°. To effect the condensation of chlorine take a bent glass tube (Fig. 37), introduce into the leg closed at one end crystals of chlorine hydrate ($Cl_2 + 10H_2O$, see below), then seal the open end. The limb containing the compound is placed in a water-bath; the other is cooled in snow. Upon heating the water a little above 30° the chlorine hydrate is decomposed into water and chlorine gas, which condenses to a liquid in the covered limb. On reversing the position of the limbs and cooling the one previously warmed, the chlorine distils back and is reabsorbed by the water. Charcoal saturated with chlorine may be substituted for the chlorine hydrate. This substance takes up 200 volumes of chlorine, which are disengaged again on heating.

Fig. 37.

One volume of water, at 20° C., absorbs 2 volumes of chlorine; at 8° C., 3 volumes. The aqueous solution is known as chlorine water (*aqua chlori*), and possesses almost all the properties of the free gas; it is therefore frequently employed for laboratory uses as a substitute for chlorine. The yellow, scale-like crystals of chlorine hydrate ($Cl_2 + 10H_2O$) separate when water saturated with the gas is cooled below 0°. This compound is regarded as one of chlorine with water. At ordinary temperatures it decomposes into water and chlorine.

Chemical Properties.—Chlorine has great affinity for almost all the elements. It combines, at ordinary temperatures, with the most of them to form chlorides; when thin sheet copper (false gold leaf), or, better, pulverized antimony or arsenic, is thrown into a vessel filled with dry chlorine, it will burn with a bright light; a piece of phosphorus will also inflame in an atmosphere of the gas.

Chlorine unites just as energetically with hydrogen. A mixture of equal volumes of the gases combines in direct sunlight, with violent explosion. In dispersed sunlight the action is only gradual; in the dark it does not occur. The great affinity of chlorine for hydrogen is manifested in the hydrogen compounds; most of these are so decomposed by the chlorine that it removes the hydrogen from them, and forms hydrochloric acid. Thus water is decomposed by chlorine into hydrochloric acid and oxygen :—

$$H_2O + Cl_2 = 2HCl + O.$$

If a glass cylinder be filled with and inverted over chlorine water and exposed to the sunlight, a gas will be evolved, and will collect in the upper portion of the vessel; this is oxygen. In diffused light the decomposition will not be so rapid; it is hastened by heat.

Chlorine, acting upon water exposed in sealed tubes to the sunlight, produces on the one hand chloric acid and hydrochloric acid, on the other hydrochloric acid and oxygen: $6Cl + 3H_2O = HClO_3 + 5HCl$; $6Cl + 3H_2O = 6HCl + 3O$. (*Annalen der Chem.*, 227, 161.)

Chlorine alters the hydrocarbons, in that it abstracts hydrogen. The reaction is sometimes so violent that carbon is separated in a free condition. A piece of tissue paper saturated with newly distilled turpentine oil, and introduced into a dry chlorine atmosphere, is immediately carbonized. An ignited wax taper immersed in chlorine burns with a smoky flame, with separation of carbon.

The organic (containing C and H) dye-stuffs are decolorized by moist chlorine gas. The same occurs with the dark-blue solutions of indigo and litmus; colored flowers are rapidly bleached by it. On this principle depends the application of chlorine in bleaching goods, and in destroying decaying matter and miasmata in chlorine disinfection. (See Bleaching Lime.)

The bleaching action of chlorine is mostly influenced by the presence of water. It probably depends on the oxidizing action of the oxygen liberated by the chlorine (see above). This property free oxygen does not possess; it does, however, very probably belong to that which is in the act of forming,—of becoming free. We will learn, later, that many other elements, at the moment of their birth (*in statu nascendi*), act more energetically than when free; the cause for this will be explained hereafter.

2. BROMINE.

$Br = 79.963$. $Br_2 = 159.926$.

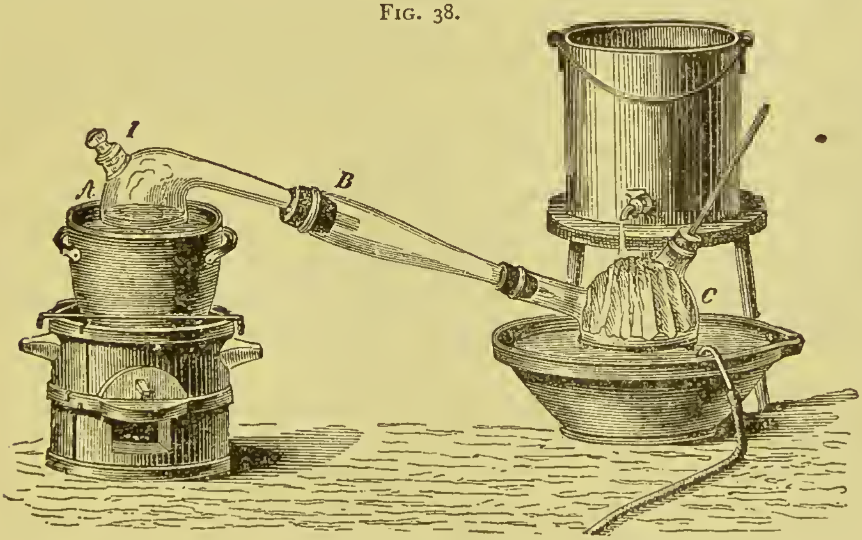
Bromine, the perfect analogue of chlorine, was discovered by Balard, in 1826. It occurs in the sea water as sodium bromide, accompanied by sodium chloride, but in much smaller quantity than the latter (especially in the water of the Dead Sea), and in many salt springs, as at Kreutznach and in Hall. When sea water or other salt water is evaporated, sodium chloride first separates; in the mother-liquor, among other soluble salts, are found sodium and magnesium bromides. Bromine is found in greatest abundance in the upper layers of the rock-salt deposits of Stassfurth, near Magdeburg, where it exists in the form of bromides together with other salts. At present, large quantities of bromine are obtained in America. The method of its preparation is similar to that employed under chlorine. A mixture of manganese dioxide and sodium bromide is warmed with sulphuric acid :—

$$MnO_2 + 2NaBr + 2H_2SO_4 = MnSO_4 + Na_2SO_4 + Br_2 + 2H_2O.$$

The operation can be executed in the apparatus pictured in Fig. 38. This can also be used for many other distillations. The retort *A*, containing the mixture, is heated in a water-bath; the tube *B* serves to cool the vapors which are condensed in the receiver *C*, surrounded by cold water or ice. When free chlorine is conducted into an aqueous solution of sodium bromide, bromine separates.

Bromine is a heavy, reddish-brown liquid, with an exceedingly penetrating, chlorine-like odor (hence the name Bromine, from *βοῶμος, stench*). At —7.3° it crystallizes to a yellow-green, scaly mass, having a metallic lustre, and resembling iodine. Liquid bromine at 0° has the specific gravity 3.18 (water = 1); it is very volatile, forming dark-brown vapors at the ordinary temperature, and boils at 63°, changing at the same time into a yellowish-brown vapor. Its density equals 79.96 (hydrogen = 1), or 5.53 (air = 1).

FIG. 38.



Bromine is more soluble in water than chlorine. Cooled below 4° C., the hydrate ($Br_2 + 10H_2O$) crystallizes out: this is analogous to the chlorine hydrate. It is decomposed at moderate temperatures. Bromine dissolves with ease in alcohol, and especially in ether, chloroform and carbon disulphide.

An aqueous solution of bromine sustains a decomposition similar to that of chlorine water on exposure to sunlight.

In a chemical point of view, bromine is extremely like chlorine, combining directly with most metals to form bromides; but it possesses a weaker affinity than chlorine, and is liberated by the latter from its compounds:—

$$KBr + Cl = KCl + Br.$$

With hydrogen it only combines on warming, not in sunlight. Upon hydrocarbons it acts like chlorine, withdrawing hydrogen from them. Bromine water gives starch an orange color.

3. IODINE.

$I = 126.86.\quad I_2 = 253.72.$

Iodine, as well as bromine, occurs in combination with sodium, in sea water and some mineral springs, especially at Hall, in Austria, and the Adelheit Spring in Bavaria. In these springs the iodine can easily be detected; in the sea water it is, however, only present in such minute quantity that its separation, practically, is disadvantageous. Sea algæ absorb it from the water, and these are then thrown by the tide on various coasts, where they are burned, yielding an ash (known as *kelp* in Scotland, as *varec* in Normandy) which is the principal source for the manufacture of iodine. It was in this ash that the element was accidentally discovered, in 1811; in 1815, it was investigated by Davy and Gay-Lussac, and its elementary character established. To obtain the iodine, the ash is treated with water, the solution concentrated, and the sodium and magnesium iodides are further worked up. Lately, iodine has been obtained from the mother-liquors of the crude Chili saltpetre. It is set free from its compounds in the same manner as chlorine and bromine—by distillation with manganese dioxide and sulphuric acid. It is more convenient, however, to pass chlorine (or better, nitrous acid) through a solution of the salt, when all the iodine will separate:—

$$KI + Cl = KCl + I.$$

The grayish-black powder thus liberated is collected on a filter, dried, and then sublimed.

Iodine is a gray-black solid, subliming in large rhombic crystals, possessing strong metallic lustre. It has a peculiar odor, reminding one somewhat of that of chlorine; it stains the skin brown, and is corrosive, although not as strongly so as bromine. Its specific gravity is 4.95. It fuses at 113° to a dark-brown liquid, and boils near 200°, passing at the same time into a dark-violet vapor (hence the name iodine, from ἰώδης, *violet-blue*).

The vapor density of iodine equals 8.7 up to 600° C. (air = 1) or 126.86 (H = 1), corresponding to the molecular weight $I_2 = 253.72$. Above 600° the vapor density gradually diminishes, and about 1500° it is only half the original. This is explained by the gradual decomposition (see Dissociation of Water) of the normal diatomic molecule I_2 into the free atoms $I + I$. In like manner the bromine molecules Br_2, suffer a separation into the free atoms. The dissociation of bromine vapor (diluted with 11 vols. of nitrogen) commences about 1000° and is complete at 1600°. The vapor density of chlorine is still normal at 1200°, and it is only at 1400° that it sustains a slight diminution. Oxygen and nitrogen on the contrary show no alteration in their vapor density even at 1690°, and possess equal power of expansion (C. Langer and V. Meyer).

Iodine is very slightly soluble in water, more readily in alcohol

(*Tinctura Iodi*), very easily in ether, chloroform and carbon disulphide, the last two assuming a deep red-violet color in consequence. It affords a particularly beautiful crystallization, consisting of forms of the rhombic system, when it separates from a solution of glacial acetic acid.

In chemical deportment iodine closely resembles bromine and chlorine; it possesses, however, weaker affinities, and for this reason is liberated from its compounds by those elements. With the metals it usually combines only when warmed; with hydrogen it does not combine directly, and it does not remove it from its carbon compounds.

The deep blue color it imparts to starch is characteristic of iodine. On adding starch-paste to the solution of an iodide, and following this with a few drops of chlorine water, the paste will immediately be colored a dark blue by the separated iodine. This reaction serves to detect the smallest quantity of it.

Iodine is largely employed in medicine, photography, and in the preparation of aniline colors.

4. FLUORINE.

$Fl = 19$. $(Fl_2 = 38.)$

Fluorine is found chiefly in the minerals fluorite ($CaFl_2$) and cryolite ($AlFl_3 . 3NaFl$). By proper treatment these minerals yield hydrofluoric acid. The latter dissolves potassium hydrogen fluoride. The resulting liquid is a good conductor of electricity, and by its electrolysis, in a U-tube of platinum, immersed during the decomposition in a bath of liquid methyl chloride, boiling at —23°, Moissan (1887) was enabled to isolate the element.

Fluorine is a greenish-yellow gas with an odor resembling that of a mixture of hypochlorous acid and nitrogen dioxide. It attacks the mucous membrane very powerfully. Its effects are very persistent. It remains as a gas at —95°, and at the ordinary pressure of the atmosphere. In the dark it unites with hydrogen with great violence, and even combines with it at —23°. It decomposes water, producing hydrofluoric acid and liberating oxygen in the form of ozone. It does not react with chlorine and nitrogen, but combines with sulphur, bromine, iodine, phosphorus, arsenic, carbon, boron, and silicon with the production of flame. Sodium and potassium unite very energetically with fluorine at the ordinary temperature. Calcium burns in an atmosphere of the gas. Iron combines with fluorine with incandescence. Lead and mercury are attacked by it in the cold. Silver is slowly attacked at the ordinary temperature. Nascent fluorine rapidly attacks platinum at a temperature of —23°, while at 100° it appears to be without action (*Ann. Chim. et Phys.*, 6th Series, 12, 472; 24, 224).

Upon the basis of theoretical observations developed later the specific gravity of free fluorine is 19 (hydrogen = 1).

These four similar elements, fluorine, chlorine, bromine, and iodine, exhibit gradual differences in their properties; and, what is remarkable, this gradation stands in direct relation to the specific gravity of the elements in the state of gas or vapor.

	Fl	Cl	Br	I
Specific gravity,	19	35.453	79.963	126.86

With the increase of specific gravity occurs a simultaneous condensation of matter, which expresses itself in the diminished volatility. Fluorine is a gas; chlorine can readily be condensed to a liquid; bromine is a liquid at ordinary temperatures, and iodine is a solid. Other physical properties, as seen in the following table, are also in accord with the preceding:—

	Fluorine.	Chlorine.	Bromine.	Iodine.
Fusing point........................	....	....	—7°	+ 113°
Boiling point........................	....	—33°	+ 63°	+ 200°
Specific gravity in liquid or solid condition........................	....	1.33	3.18	4.97
Color........................	Green-yellow	Yellow	Brown	Black

Just such a gradation, as we have seen, is observed in the chemical affinities of these four elements for the metals and hydrogen; fluorine is the most energetic, iodine the least. Therefore, each higher element is separated from its soluble metallic and hydrogen compounds by the lower. We shall discover, later, that in the affinity-energy of the halogens for oxygen and some other metalloids, the reverse is true.

COMPOUNDS OF THE HALOGENS WITH HYDROGEN.

With hydrogen the halogens form compounds of an acid nature, readily soluble in water.

1. HYDROGEN CHLORIDE.

$HCl = 36.456$. Density $= 18.22$.

The direct union of chlorine with hydrogen takes place through the agency of heat, and by the action of direct sunlight or other chemically active rays; in diffused light the action is only gradual, and does not occur at all in the dark. On introducing a flame of hydrogen ignited in the air into a cylinder filled with chlorine (Fig. 39), it will continue to burn in the latter. The opposite, the combustion of chlorine in an atmosphere of hydrogen, may be shown easily by the following experiment (Fig. 40). An inverted cylinder is filled with hydrogen by displacement, the gas is ignited at the mouth, and a tube immediately introduced which will conduct dry chlorine into the cylinder. The burning hydrogen will inflame the chlorine, which will continue to burn in the former. From these experiments, we perceive that combustibility and combustion are only relative phenomena; if hydrogen is combustible in chlorine (or air), so, inversely, is chlorine (or air) combustible in hydrogen. By the term combustion, in chemistry, is understood every chemical union of a body with a gas, which is accompanied by the phenomenon of light.

A mixture of equal volumes of chlorine and hydrogen explodes with very great violence under the conditions given above for the union of the gases. The product is gaseous hydrogen chloride.

FIG. 39.

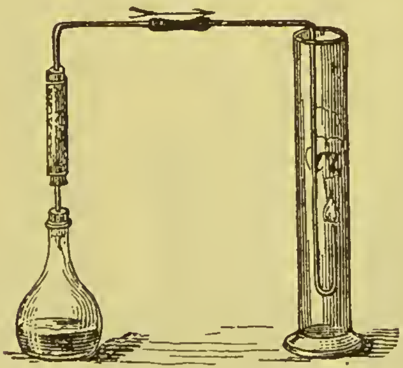


FIG. 40.

The formation of the latter compound succeeds best by allowing sulphuric acid to act upon sodium chloride, when solid sodium sulphate and hydrogen chloride gas will result:—

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

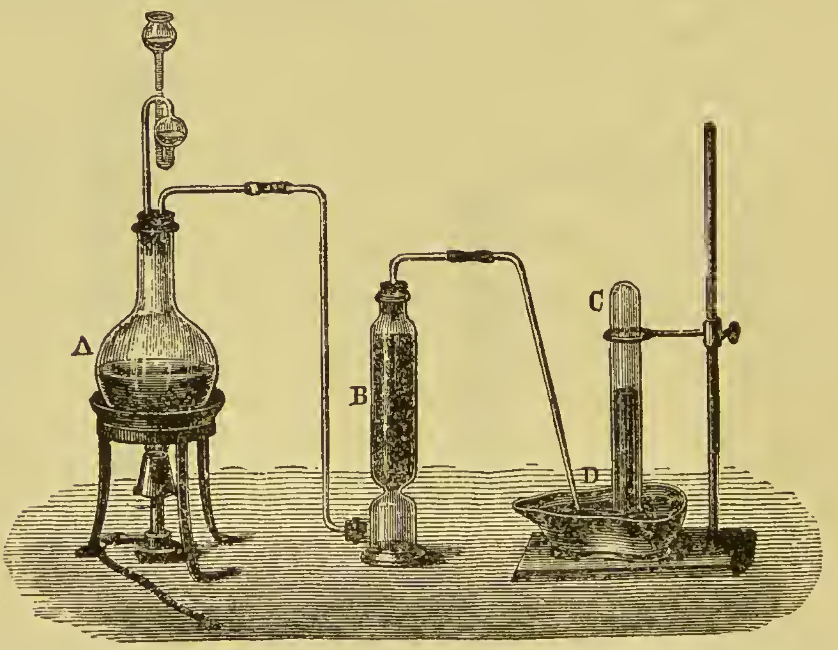
Pour over 5 parts sodium chloride, 9 parts sulphuric acid, somewhat diluted with water (2 parts), and warm the mixture gently in a flask, A (Fig. 41). The escaping hydrogen chloride is conducted through a Woulff's bottle containing sulphuric acid or through the cylinder B (filled with pumice stone saturated with sulphuric acid), intended to free it from all moisture, and afterward collected over mercury.

Physical Properties.—Hydrogen chloride is a colorless gas, with a suffocating odor. In moist air it forms dense clouds. Its critical temperature is about + 52.3°, and the critical pressure 86 atmospheres, *i. e.*, for its condensation at the temperature just given it requires a pressure of 86 atmospheres. There is no pressure which will condense it above this temperature. Liquid hydrogen chloride is colorless. Its sp. gr. is 1.27. It boils at —80.3° under a pressure of 1 atmosphere, but does not solidify at —110°.

The specific gravity (density) of the gas is 18.22 (H = 1), or 1.26 (air = 1).

Hydrogen chloride possesses an acid taste, and colors blue litmus paper red; it is, therefore, an acid, and has received the name hydrochloric acid gas. It dissolves very readily in water, and on that account cannot be collected over it. One volume of water at 0° C., dissolves 505 volumes, and at ordinary temperatures about 450 volumes of the gas. This great solubility is very nicely illustrated by filling a long glass cylinder with the gas and then just dipping its open end into water; the latter rushes up into the vessel rapidly (as into a vacuum), as it quickly absorbs the gas. The aqueous solution of hydrogen chloride, in ordinary language, is known as muriatic or hydrochloric acid (*Acidum hydrochloratum*). For its preparation the gas is passed through a series of Woulff bottles (Fig. 42) containing water. The small bottle *B*, in which there is but little water, serves to wash the gas—free it of any mechanically admixed sulphuric acid. The same apparatus may be employed in

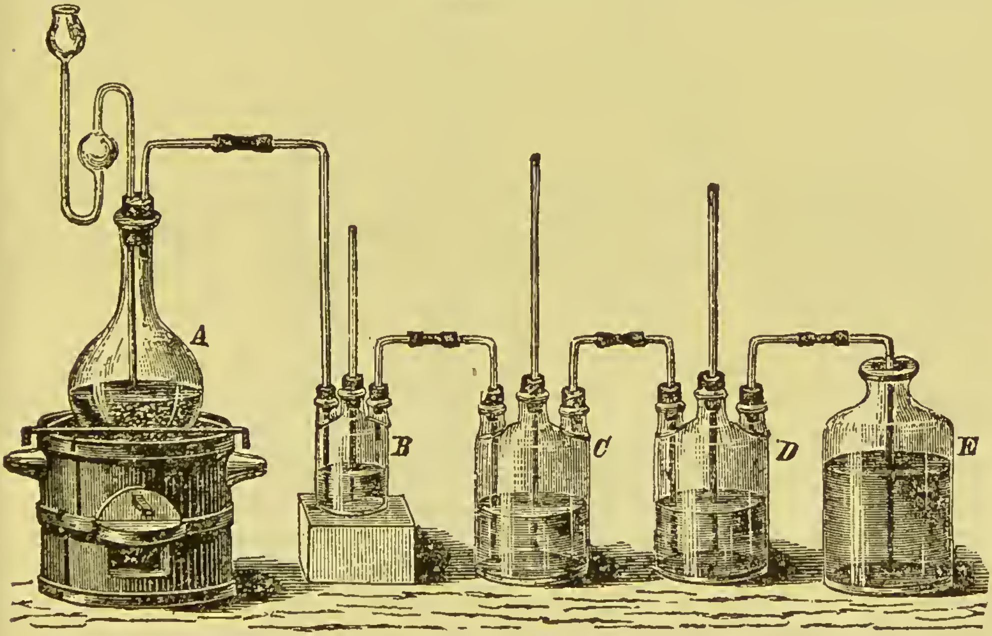
FIG. 41.



the manufacture of chlorine water, and is generally used in the saturation of liquids with gases.

A solution saturated at 15° C., contains about 42.9 per cent. hydrogen chloride, has a specific gravity of 1.2, and fumes in the air. On the application of heat, the gas again escapes, and the temperature of the liquid rises to 110° C., when a liquid distils over, containing about 20 per cent. of hydrogen chloride, having a specific gravity of 1.104 and almost corresponds to the formula $HCl + 8H_2O$. The composition of the distillate varies somewhat with the pressure. On conducting hydrogen chloride into hydrochloric acid cooled to —22°, crystals of the formula $HCl + 2H_2O$ separate; these fuse at —18° and then decompose.

FIG. 42.



Hydrochloric acid finds an extensive industrial application, and is obtained in large quantities, as a by-product, in the soda manufacture.

Chemical Properties.—Acids—Bases—Salts.—Hydrogen chloride, as well as its solution, possesses all the properties of *acids*, and can well figure as a prototype of these; it tastes intensely acid, reddens blue litmus paper, and saturates the *bases* (oxides and hydroxides), *i. e.*, such bodies as impart a blue color to red litmus paper. If we add hydrochloric acid to a solution of a base, *e. g.*, sodium hydroxide, until the reaction is neutral, we will obtain (besides water) a neutral, solid compound—sodium chloride.

$$NaOH + HCl = NaCl + H_2O.$$

Sodium hydroxide. Sodium chloride.

HBr, HI, and HFl deport themselves similarly to HCl. These halogen compounds of hydrogen are termed *haloid acids*, to distinguish them from those which, in addition to hydrogen, contain oxygen, hence called *oxygen acids*. The latter conduct themselves like the former, and saturate bases, forming salts and water:—

$$KOH + HNO_3 = KNO_3 + H_2O.$$

Potassium hydroxide. Nitric acid. Potassium nitrate. Water.

In the same manner the acids act upon the basic oxides, to form salts and water:—

$$ZnO + 2HCl = ZnCl_2 + H_2O.$$

Zinc oxide. Zinc chloride.

$$ZnO + 2HNO_3 = Zn(NO_3)_2 + H_2O.$$

Zinc oxide. Zinc nitrate.

Usually when acids act upon metals, the hydrogen of the former is directly displaced; *salts* and free hydrogen are produced. Thus, by the action of hydrochloric acid upon sodium, its chloride and hydrogen result:—

$$HCl + Na = NaCl + H.$$

From the examples cited it is manifest that *acids* are hydrogen compounds which yield *salts*, by the replacement of their hydrogen by metals (by the action of metallic oxides, hydroxides, and by the free metals). The metallic oxides and hydroxides capable of forming salts by the saturation of acids are called *bases*. Finally, by the term *salts*, we understand such compounds as are analogous to sodium chloride, and are formed by the mutual action of bases and acids. Salts are distinguished as *haloid salts* and *oxygen salts*. The first have no oxygen, and arise in the direct union of the halogens with the metals.

Hydrogen chloride is a very stable compound, suffering only a partial decomposition at 1500° C. Its composition is easily established analytically by the following experiments: Pass hydrochloric acid gas over a piece of sodium or potassium, heated in a glass tube, and hydrogen will escape from the latter:—

$$Na + HCl = NaCl + H.$$

If manganese peroxide, on the other hand, be heated in it, chlorine will be disengaged:—

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

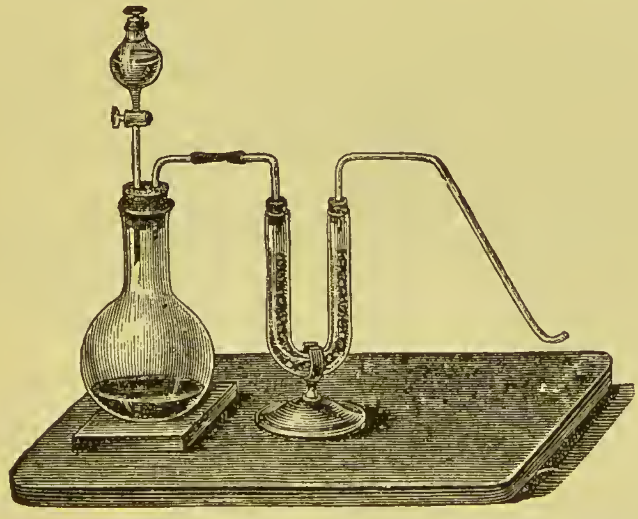
If the electric current be permitted to act upon an aqueous solution of hydrochloric acid, the latter will be so decomposed that chlorine separates at the electro-positive and hydrogen at the electro-negative pole. (See p. 75.)

2. HYDROGEN BROMIDE.

$HBr = 80.966$. Density $= 40.48$.

Hydrogen bromide is perfectly similar to the corresponding chlorine compound. As there is but slight affinity between Br and H their direct union will only occur at a red heat or in the presence of platinum sponge. (See p. 46.) Like hydrogen chloride, hydrogen bromide can be obtained by the action of some acids, *e. g.*, phosphoric acid, upon bromides; sulphuric acid would not answer as the resulting HBr is again partly decomposed by it.

FIG. 43.



Ordinarily it is prepared by the action of phosphorus tri-bromide (see Phosphorus) upon water:—

$$\underset{\text{Phosphorus tri-bromide.}}{PBr_3} + 3H_2O = \underset{\text{Phosphorous acid.}}{H_3PO_3} + 3HBr.$$

Place some water (1 part) in a flask (Fig 43), gradually admit through the funnel, supplied with a cock, the liquid PBr_3 (3 parts), and warm gently. The escaping HBr gas is collected over mercury or conducted into water. To free it perfectly from accompanying PBr_3 vapors it is passed through water (the U-shaped tube in Fig. 43 contains pieces of pumice stone, which are moistened with water).

Instead of employing prepared brom-phosphorus, we may let bromine vapors act upon (red) phosphorus. This may be done by pouring water or dilute hydrobromic acid (2 parts) over the phosphorus placed in a flask. Bromine (10 parts) is added gradually while cooling and heat then applied. To free the HBr gas from the bromine carried along mechanically, conduct it through a tube containing moist phosphorus.

Gaseous hydrobromic acid can also be prepared by allowing bromine to act upon crude anthracene. The resulting hydrobromic acid gas is freed from the accompanying bromine by passing it through a tube filled with anthracene.

To obtain an aqueous solution of the gas, pour 15 parts H_2O over 1 part amorphous phosphorus, and then add Br (10 parts) drop by drop. Finally the solution is heated, filtered, and distilled. From bromides (NaBr, KBr) hydrogen bromide is obtained by distillation with somewhat dilute sulphuric acid, with addition of phosphorus.

Hydrogen bromide is a colorless gas, fuming strongly in the air. Under great pressure it is condensed to a liquid, boiling at —73.3° and solidifying at —120°. Its density is 40.38 ($H = 1$) or 2.79 ($air = 1$).

In water the gas is very readily soluble, its saturated solution having a specific gravity of 1.78, and containing 82 per cent. HBr; at 15° it contains 49.8 per cent., and has the specific gravity of 1.515. At 125° C., a solution distils over containing 46.8 per cent. HBr, and closely approximates the formula $HBr + 5H_2O$; its specific gravity is 1.47 at 14° C.

On conducting HBr into a solution of the same cooled to —20°, crystals of the formula $HBr + 2H_2O$ separate and melt at —11°. Chemically, HBr is the perfect analogue of HCl; it is, however, less stable, and suffers a partial decomposition at 800° C.

3. HYDROGEN IODIDE.

$HI = 127.863$. Density $= 63.93$.

The attraction of iodine for hydrogen is very slight. Their partial union occurs when both elements, in the form of vapor, are conducted over platinum sponge. It cannot be obtained by acting upon iodides with sulphuric acid, because the resulting hydrogen iodide decomposes more easily than the bromide. It is formed, however, similarly to the latter, by acting on phosphorus iodide with water:—

$$PI_3 + 3H_2O = PO_3H_3 + 3HI.$$

A more convenient procedure is to warm a mixture of amorphous phosphorus (1 part), iodine (15 parts), and water (14 parts); when an analogous reaction will ensue. Or add a solution of 2 parts iodine in 1 part hydriodic acid, of specific gravity 1.67 (obtained by distillation, see below), drop by drop, to red phosphorus, and aid the reaction by heat. As HI dissolves readily in water, and is decomposed by mercury, we can only collect it by conducting it into a dry flask (Fig. 44), where it will displace the air in consequence of its fivefold greater density.

To get an aqueous solution of HI, take more water, warm the solution, filter, and then distil.

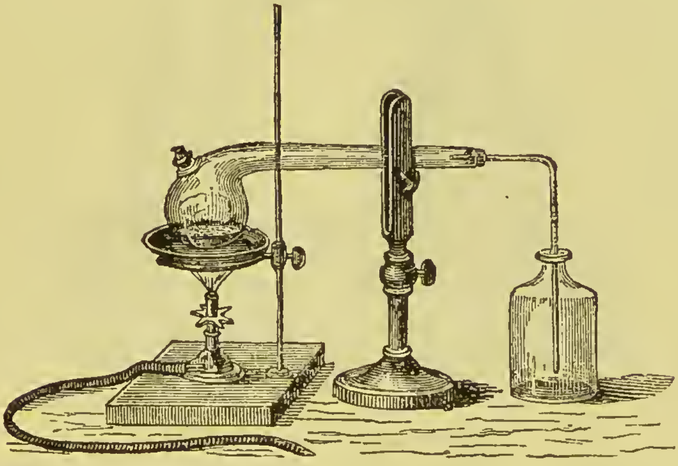
Another method for obtaining HI consists in passing hydrogen sulphide into water to which finely pulverized iodine is added, until there is no further decolorization :—

$$H_2S + I_2 = 2HI + S.$$

Filter off the separated sulphur and distil the liquid.

Hydrogen iodide is a colorless gas; it fumes strongly in the air; its density is 63.7 ($H = 1$) or 4.41 ($air = 1$). Under a pressure of 4 atmospheres (at 0°) it is condensed to a liquid which solidifies at —55°. It is easily soluble in water, 1 vol. of the latter dissolving 427 vols. of the gas at 10°. The solution saturated at 0° C., has a specific gravity 1.99, and fumes strongly in the air. At 127° a solution of 1.67 specific gravity, and containing 57.7 per cent. HI, distils over, corresponding closely to the formula $HI + 5H_2O$.

FIG. 44.



Hydrogen iodide is a rather unstable compound, decomposing at 180° into hydrogen and iodine (see dissociation of water). At high temperatures oxygen decomposes it into water and iodine :—

$$2HI + O = H_2O + I_2.$$

On bringing a flame near a vessel containing a mixture of HI and oxygen, violet iodine vapors will at once fill it. The same will be noticed when fuming nitric acid is dropped into a vessel containing HI; in this reaction the oxygen of the acid oxidizes the hydrogen and liberates iodine. All oxidizing bodies behave in the same way; the hydrogen iodide abstracts their oxygen and reduces them. The oxygen of the air, even at the ordinary temperature, and especially in sunlight, gradually decomposes aqueous hydrogen iodide. The solution, at first colorless, becomes brown, owing to separation of iodine, which in the beginning dissolves; subsequently, however, it separates in beautiful crystals.

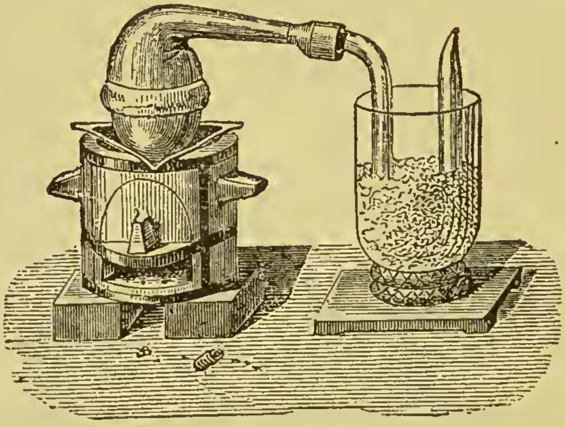
At ordinary temperatures mercury and silver decompose HI, with separation of hydrogen:—

$$HI + Ag = AgI + H.$$

Chlorine and bromine liberate iodine from HI.

This compound is employed as a powerful reducing agent in laboratory work.

Fig. 45.



4. HYDROGEN FLUORIDE.

$HFl = 20$. Density $= 10$ (at 100°).

It is obtained, like hydrogen chloride, by decomposing fluorides with sulphuric acid. Finely pulverized fluorite is mixed with H_2SO_4 and heat applied gently:—

$$\underset{\text{Calcium fluoride.}}{CaFl_2} + H_2SO_4 = \underset{\text{Calcium sulphate.}}{CaSO_4} + 2HFl.$$

The operation is executed in a lead or platinum retort, as the hydrogen fluoride attacks glass and most of the metals. (Fig. 45.) The escaping HFl condenses in the U-shaped receiver containing water. To get perfectly anhydrous hydrogen fluoride, heat hydrogen potassium fluoride, which then decomposes according to the following equation:—

$$KFl_2H = KFl + HFl.$$

Anhydrous hydrogen fluoride is a colorless, very mobile liquid, fuming strongly in the air, and attracting moisture with avidity; it boils at + 19° C., and has a specific gravity of 0.98 at 12°. To recondense the gas it must be cooled to —20°.

The gas density of hydrogen fluoride equals 10 (hydrogen = 1) at 100°, corresponding to the molecular formula HFl = 20. At 30°, however, it is twice as large, equaling 20. It follows, therefore, that the molecules of the gas at the latter temperature correspond to the formula H_2Fl_2, and consist of two chemical molecules of HFl. (Compare arsenic trioxide.)

The concentrated aqueous solution fumes in the air; when heated HFl escapes; the boiling temperature increases regularly and becomes constant at 120° C., when a solution distils over, the specific gravity of which is 1.15, and its percentage of HFl 35.3. The vapors as well as the solution are poisonous, extremely corrosive, and produce painful wounds upon the skin.

Hydrofluoric acid dissolves all the metals, excepting lead, gold and platinum, to form fluorides. It decomposes all oxides, even the anhydrides of boric and silicic acids, which it dissolves to form boron and silicon fluorides. Glass, a silicate, is also acted upon; hence the use of the acid for etching this substance. (Compare silicon fluoride.) To do this, coat the glass with a thick layer of wax or paraffin, draw any figure upon it with a pin, and then expose it to the action of the gaseous or liquid HFl. The exposed portions appear etched; gaseous HFl furnishes a dim, and liquid HFl a smooth, transparent etching.

Vessels of lead, platinum, or caoutchouc are employed for the preservation of hydrofluoric acid, as they are not affected by it.

These halogen derivatives of hydrogen show great resemblance to each other. At ordinary temperatures they form strongly smelling and fuming gases, which by pressure can be condensed to liquids. Their fuming in moist air is due to the fact that they are condensed by the aqueous vapor. Readily soluble in water, they are only partially expelled from their saturated solution by boiling; when solutions of definite composition distil over: these may be regarded as chemical combinations of the halogen hydrides with water. As acids they neutralize the bases and form haloid salts, which also result by the direct union of the halogens with metals.

The densities of the halogen hydrides exhibit a gradation similar to that of the densities of the halogens (page 56):—

	HFl	HCl	HBr	HI
Density,	10	18.22	40.48	63.93.

The difference in chemical deportment corresponds to this gradation. Hydrogen fluoride is the most stable, and acts most energetically; chlorine combines with hydrogen in sunlight, bromine only at a red heat, while iodine and hydrogen do not react at all. On the other hand, hydrogen iodide is decomposed at a gentle heat (180°), into its constituents; the more stable hydrogen bromide at 800°, while hydrogen chloride remains unaltered up to 1500° C. Corresponding to this we have the very energetic action of fluorine, and the tolerably ready action of chlorine upon water, oxygen separating at the same time:—

$$H_2O + Cl_2 = 2HCl + O.$$

Iodine does not act upon water. The opposite reaction occurs: oxygen decomposes hydrogen iodide into water and iodine:—

$$2HI + O = H_2O + I_2.$$

Bromine occupies an intermediate position between chlorine and iodine; in dilute aqueous solution it decomposes water into $HBr + O$, while a concentrated solution of hydrogen bromide, on the contrary, is partly decomposed by oxygen into water and free bromine.

From all the above it is evident that the affinity of fluorine for hydrogen is the greatest; then follow chlorine and bromine, and finally, as the least energetic element, we have iodine. (See p. 56.)

THERMO-CHEMICAL DEPORTMENT OF THE HALOGENS.

The quantities of heat, disengaged or absorbed in chemical reactions (p. 27), afford the most satisfactory explanations of the deportment of the halogens with hydrogen, and indeed of all the chemical elements and compounds toward each other. These heat changes are also called *positive* and *negative* thermal values (*heat modulus*).

The quantities of heat are estimated in *heat units* or *calories*. The quantity of heat required to raise 1 gram of water from 0° to 1° C., is taken as the *heat unit*. As the numbers obtained in this way are very large, and since the last two places are not correct, but fall within the error limit, they are disregarded, and the calorie is considered as that quantity of heat which will raise 1 kilogram of water 1° C. These *large* or *great* calories will be employed in the following pages.

To obtain data that may be easily compared, the quantities of heat are not referred to 1 gram of the various substances, but to quantities in grams corresponding to the atomic weights of the elements entering into combination. Thus in the union of 35.45 gr. of chlorine (Cl) with 1 gr. of hydrogen (H) to form 36.45 gr. hydrogen chloride (HCl), 22.0 Cal. are set free, and when 79.96 gr.

bromine combine with 1 gr. of hydrogen to form hydrogen bromide 8.4 Cal., are developed, while in the union of 126.5 gr. iodine with 1 gr. hydrogen 6.0 Cal., are absorbed.

This may be expressed according to the method of J. Thomsen, as follows:—

$$(H,Cl) = + 22.0 \text{ Cal.}; \quad (H,Br) = + 8.4 \text{ Cal.}; \quad (H,I) = - 6.0 \text{ Cal.}$$

The first two reactions, in which heat is liberated, are exothermic, while the heat-absorbing combination of iodine with hydrogen represents an endothermic reaction (see p. 28). The energy-content of HCl and HBr is less, and that of HI greater than that of their components.

The quantity of heat disengaged in a combination may be regarded as a measure (relative) of the chemical affinity. As the elements do not exist as free atoms, but as molecules these require a definite quantity of heat to decompose them into atoms before they can enter into chemical reaction. This necessitates a definite amount of work (addition of energy). The union of chlorine with hydrogen proceeds according to the molecular equation (p. 78):—

$$HH + ClCl = 2HCl.$$

The heat here disengaged (2 × 22.0 calories) indicates that the affinity of 2H for 2Cl is just that much greater than the affinity of H for H + Cl for Cl in their molecules. $(H, H) + (Cl, Cl) = 2\ (H, Cl) \ldots + 2 \times 22.0$ Cal. Similarly, the heat absorbed in the formation of hydrogen iodide, shows that the affinity of I for H is less than that of the atoms H and I in their molecules.

It is very probable that the union of the free atoms always occurs with heat-disengagement, and the heat absorbed in combining is invariably caused by antecedent decompositions.

The greater the heat developed in a reaction, the more energetically and the more readily will it occur, and in general, the resulting compounds will be the more stable. In accordance with this, as we have seen, chlorine and hydrogen unite readily with each other producing stable hydrogen chloride, which only sustains a slight decomposition at 1500°. In the union of hydrogen and iodine, where heat is absorbed, the combination occurs with difficulty, and can only be effected by the constant addition of energy (heat). The resulting hydrogen iodide is an endothermic compound, and is very unstable, decomposing at 180°. Since iodine and hydrogen will only unite at high temperatures, their union is restricted by the power of dissociation possessed by the HI, and it is therefore only a partial union. Hydrogen bromide occupies a position intermediate between HCl and HI. This accords with and might be expected from its heat of formation. The principle of greatest heat development also accounts for the displacement of iodine from its combinations by chlorine and bromine, and bromine by chlorine—corresponding to the following thermo-chemical equations:—

$$\underset{(-6.0)}{HI} + Cl = \underset{(22.0)}{HCl} + I \ldots (+ 28 \text{ Cal.})$$

$$\underset{(8.4)}{HBr} + Cl = \underset{(22.0)}{HCl} + Br \ldots (+ 13.6 \text{ Cal.})$$

The thermo-chemical sign of a reaction is obtained by deducting from the heat of formation of the products that of those reacting. Conversely, from the thermal value of the reaction determined experimentally, we may ascertain the heat of formation of one of the reacting or resulting bodies.

Remembering the thermal relations in the formation of water, we can explain in the same manner, the varying decomposition of the halogen hydrides by oxygen, and the reverse—that of water by the halogens. The *heat of formation* of water from its elements equals 57.2 Cal., if it be in the gaseous state, but when it is as a liquid it is 68.3 Cal.: (H_2,O) vapor $= 57.2$. (H_2,O) liquid $= 68.3$. As the heat of formation of 1 eq. of H_2O 28.6 $(= \frac{57.2}{2})$, is greater than that of 1 eq. of the halogen hydrides (see above), oxygen will displace chlorine, iodine and bromine from their hydrogen derivatives and the energy of displacement will be in proportion to the difference there is in the heat of formation.

In fact, we observed that when a flame, or some glowing substance, was brought in contact with a mixture of hydrogen iodide and oxygen, all the iodine was separated in the form of vapor, in accordance with the following equation:—

$$2HI + O = H_2O \text{ (vapor)} + 2I \quad . \ . \ . \quad (+ 69.2 \text{ Cal.})$$

Oxygen also liberates bromine from hydrogen bromide at a temperature of about 500° (neither HBr nor water suffer dissociation at this temperature). Aqueous vapor is also produced.

The action proceeds with more difficulty, however, in the case of oxygen and hydrogen chloride, which is no doubt to be attributed to the slight difference in their *heats of formation*:—

$$2HCl + O = H_2O + Cl \quad . \ . \ . \quad (+ 13.2 \text{ Cal.})$$

Only a partial transposition into chlorine and aqueous vapor occurs upon conducting a mixture of HCl and O through a tube raised to a bright red heat. This is evident because water below 1000° sustains only a partial decomposition, and chlorine not any until a temperature of 1500° has been reached (p. 67). At the temperature of the reaction the water is partly converted into oxygen and hydrogen, when the latter unites with the chlorine. If aqueous vapor and chlorine are passed through a tube heated to redness, the opposite reaction takes place; hydrogen chloride and oxygen result. Both reactions, however, are very incomplete and mutually limit each other (inverse reactions).

The greater stability of hydrogen chloride, as compared with water, also explains why, in a mixture of hydrogen, oxygen, and chlorine, the hydrogen first combines with the chlorine and afterward with the oxygen, although the heat of formation of water is greater than that of hydrogen chloride.

The deportment of oxygen towards the halogen hydrides is somewhat different when the latter are in aqueous solution. The same may be remarked of the behavior of the halogens towards water in liquid state. In these cases we must bring into consideration the *heat of solution* of the halogen hydrides. It corresponds to the symbols:—

$$(HCl,Aq) = 17.3; \ (HBr,Aq) = 19.9; \ (HI,Aq) = 19.2.$$

The heat of formation of the halogen hydrides from the elements when in dilute aqueous solution will therefore equal:—

$$(H,Cl,Aq) = 39.3; \ (H,Br,Aq) = 28.3; \ (H,I,Aq) = 13.2.$$

In accord with these heats of formation, we discover that the oxygen of the air at the ordinary temperature (in sunlight) gradually liberates the iodine from aqueous hydrogen iodide, water forming at the same time. This corresponds to the thermochemical equation:—

$$2(HIAq) + O = H_2O\text{-liquid} + 2I \quad . \ . \ . \quad (+ 41.9 \text{ Cal.})$$

Iodine, on the other hand, does not act upon water. Oxygen cannot affect aqueous hydrogen chloride, but water may be decomposed gradually by chlorine into hydrochloric acid and oxygen (p. 52) according to the equation:—

$$H_2O\text{-liquid} + 2Cl = 2(HClAq) + O \quad . \ . \ . \quad (+ 10.3 \text{ Cal.})$$

As far as water is concerned, bromine holds an intermediate position between chlorine and iodine (p. 66).

To illustrate these interesting relations, let us study the formation of hydrogen iodide by the action of iodine upon hydrogen sulphide (p. 63). Since the heat of formation of 2HI (gas) (— 12.0) is less than that of H_2S-gas (+ 4.5), it is impossible for iodine to act upon gaseous hydrogen sulphide:—

$$H_2S + I_2 = 2HI + S \ . \ . \ . \ (-7.5 \text{ Cal.})$$

In presence of water the result is different. Aqueous HI is formed; its heat of formation (2 × 13.2 Cal.) is greater than that of the aqueous H_2S-water (9.2 Cal.):—

$$H_2S\,Aq + 2I = 2HIAq + S \ . \ . \ . \ (+17.2 \text{ Cal.})$$

The transposition is incomplete if the quantity of water is small.

COMPOUNDS OF THE HALOGENS WITH EACH OTHER.

These compounds, formed by the union of the halogens with each other, are very unstable, and it may be remarked here, that this is also true of most derivatives obtained from elements which are similar in chemical respects.

When chlorine is conducted over dry iodine, the latter being in excess, mono-chlor-iodine results, and when the chlorine is in excess, trichlor-iodine is formed

Iodine Chloride—ICl—is a red crystalline mass, fusing at 24.7° C., and distilling a little above 100° C. Water decomposes it easily, with formation of iodic acid, iodine, and hydrogen chloride.

Iodine Trichloride—ICl_3—is formed upon mixing iodic acid with concentrated hydrochloric acid, and by the action of PCl_5 upon I_2O_5. It crystallizes in long, yellow needles, and, when heated, suffers decomposition into ICl and chlorine (at ordinary pressure, the dissociation commences at 25° C.). It dissolves in a little water without alteration; but large quantities cause partial decomposition, with formation of iodic acid.

Iodine Bromide—IBr—obtained by the direct union of the elements, consists of iodine-like crystals, fusing at about 30°.

Iodine Pentafluoride—IFl_5—is produced by the action of iodine upon silver fluoride, and forms a colorless, strongly fuming liquid.

WEIGHT PROPORTIONS IN THE UNION OF THE ELEMENTS. THE LAW OF CONSTANT PROPORTIONS. ATOMIC HYPOTHESIS.

If in the halogen derivatives considered, as well as in all other chemical compounds, we determine the quantity of the elements (according to methods described in analytical chemistry), we will discover that they are always combined with each other in the same proportions by weight. *In every chemical compound the proportions by weight of the constituents contained in it are invariably the same.* Thus chemical analysis shows the following percentage composition for the halogen derivatives of hydrogen :—

H = 5.0	H = 2.7	H = 1.2	H = 0.8
Fl = 95.0	Cl = 97.3	Br = 98.8	I = 99.2
HFl = 100.0	HCl = 100.0	HBr = 100.0	HI = 100.0

Experience has shown that hydrogen, of all the elements, enters compounds in the least quantity, therefore its quantity is chosen as unity, and we calculate those weights of the elements which combine with one part by weight of H. In this manner we find the following proportions for the halogens :—

H = 1	H = 1	H = 1	H = 1
Fl = 19	Cl = 35.45	Br = 79.96	I = 126.86
HFl = 20	HCl = 36.45	HBr = 80.96	HI = 127.86

Experiments have also established the remarkable fact that the same proportions of the halogens by weight are also obtained by the union of the same with other elements. Thus 19 parts of Fl by weight combine with the following weights of the metals: 23.06 parts Na, 39.14 parts K, 32.7 parts Zn, 31.6 parts Cu, 100.2 parts Hg, and 35.45 parts Cl, 79.96 parts Br, and 126.8 parts I combine with exactly the same quantities of these metals by weight. Let us take another example. On bringing copper into the solution of a mercuric salt the former dissolves, while Hg separates out; indeed, 31.6 parts Cu displace 100.2 parts Hg. If zinc be brought into the copper solution thus obtained, it will dissolve, while copper separates—and 32.7 parts of Zn separate 31.6 parts Cu. Furthermore, zinc displaces the hydrogen in acids; from all of them 32.7 parts Zn separate 1 part H. In all these reactions we observe the elements appearing in the same quantities by weight.

These remarkable facts are fully verified by experiments. Such facts may be formulated into a *rule*, and when a rule comprises a great number of facts—true for all and expressible in numbers—we designate it a *law*. The facts presented above find their expression in the empirical *law of constant proportions*, first proposed by Dalton, and reading: The elements combine with each other in definite proportions by weight; and the proportions by weight of two elements remain the same in their combinations with other elements.

Causes underlie facts. The cause is first expressed in the form of a supposition or *hypothesis*, and when the latter includes a long series of facts, if it is repeatedly substantiated by other phenomena and has acquired a high degree of probability, it is termed a *theory.*

If an hypothesis completely satisfies all the observations to which it refers, it becomes a fact, for the further explanation of which a new hypothesis may be necessary. Conversely, something which long passed as a fact or a theory may be shown to be erroneous, if not any longer consistent with new observations. Hypothesis and that which we designate a fact, are distinguished really by the different degree of probability only. If, for example, we make a sight observation we assume the hypothesis that the same has been caused by an external process, of the reality of which (in distinction from subjective perceptions) we can only assure ourselves by repeated observations. The hypothesis of the revolving of the earth, which at first was only a suitable, improbable supposition, proposed for simplifying calculation, has become a fact. The combustion theory of Lavoisier met a like result. The same may be true with regard to the supposition of atoms—whether we comprehend them as material particles or as ether motion.

The law of constant proportion finds its clearest explanation in the *hypothesis of the existence of atoms.* Grecian philosophers even conjectured that matter consisted of indivisible and very small particles—*atoms* (from ἀ, privative, and τόμος, division). This *a priori* supposition was subsequently repeatedly announced, but Dalton (1804) first gave it an actual confirmation, in that he applied it to the law of constant proportions. According to the atomic view, matter consists of extremely small (although not indefinitely small) particles, atoms, which cannot be further divided, either mechanically or chemically. The atoms of different elements possess different weights; all atoms, however, of one element have the same absolute weight and are like each other. By the aggregation of the elementary atoms arise the smallest particles of compound bodies. Upon the basis of these representations, the law of constant proportions becomes very simple; we can comprehend that the quantities of the constituents of a compound should be constant, and that the relative quantities of the elements by weight, must be the same in all their compounds, as they express the relative weights of the atoms.

As yet only the relative atomic weights of the elements have been determined by chemical researches; in these the hydrogen atoms, as they possess the least weight, have been taken as unity. Until now the knowledge of the absolute atomic weight, for chemical considerations, has been unessential. At the present time different physical phenomena permit fixing the absolute size of the atom with considerable approximate accuracy. Very different considerations lead to the same conclusion, that the atoms cannot be smaller than the fifty-millionth part of a millimeter. (Thomson.) We can determine the diameter of the molecules more accurately with the gases. With hydrogen H_2 it has been found equal to the 4 —, with N_2 the 3 —, with O_2 the 7 — 10-millionth part of a millimetre.

If we grant that in the preceding halogen-hydrogen compounds one atom of hydrogen is combined with every halogen atom, the conclusion follows, that the ratio found expresses the relative atomic weights of the halogens. This supposition, however, appears questionable, in view of the more complicated proportions which occur in the union of some elements. Observation shows, to wit, that very frequently two elements unite with each other in not only one, but, indeed, several proportions. For example, 35.45 parts of chlorine combine not only with 31.6 parts copper and 100.2 parts mercury, but also with 63.3 parts copper and 200.4 parts mercury. One part, by weight, of hydrogen, combines with 8 parts of oxygen (more accurately 7.98) to form water, and with 16 parts oxygen (to form the so-called hydrogen peroxide); further, with 16 and 32 parts sulphur. Oxygen forms five different compounds with nitrogen according to the following proportions by weight:—

	Nitrogen.	Oxygen.
Nitrous oxide, ...	14 parts.	8 parts = 1 × 8.
Nitric oxide, ...	14 parts.	16 parts = 2 × 8.
Nitrous anhydride, . . .	14 parts.	24 parts = 3 × 8.
Nitrogen dioxide, . . .	14 parts.	32 parts = 4 × 8.
Nitric anhydride, . . .	14 parts.	40 parts = 5 × 8.

Similar proportions are observed in the union of many other elements. Therefore, they combine with each according to several ratios by weight. As we have noticed in the examples given, the varying quantities of one of the elements (calculating upon the same quantity of the other element), bear a simple ratio to each other; they are mostly multiples of the smallest quantity. These facts are enunciated in the *Law of Multiple Proportions*, also proposed by Dalton (1807), which forms an essential amplification of the law of constant proportions. Based on the atomic hypothesis, these facts are explained by saying that the elements can not only unite with each other, atom for atom, but in variable quantities. This considerably complicates the problem of determining the relative atomic weights of the elements, as these are directly dependent upon the conceived number of atoms in a compound. If, for example, in water, one atom of hydrogen is combined with one atom of oxygen, the atomic weight of the latter would = 8 (regarding that of hydrogen as 1). It is just as likely that water consists of two atoms of H and O, or of one of H and two of O, etc.; in the first case the atomic weight of O would = 16, in the latter, 4.

Analytical results afford nothing positive for the solution of this difficulty. This was the condition in which the question relating to the magnitude of the atomic weights existed thirty years ago. To establish these correctly, various views were allowed to prevail, none, however, with positive foundation. The question can only be solved upon a new and accurate basis: the specific gravities of the chemical compounds in a gaseous or vapor form answer well for this purpose.

DENSITIES OF BODIES IN STATE OF GAS. VOLUME RATIO IN THE UNION OF GASES. ATOMIC MOLECULAR THEORY.

The halogens, fluorine, chlorine, bromine, and iodine, unite with hydrogen in only one proportion. The supposition, therefore, that in the halogen-hydrogen compounds, 1 atom of H is combined with 1 atom of the halogen, is the simplest and most probable. Then their weight proportions, derived from analysis, directly express their relative atomic weights. By comparing these atomic numbers (referring to H = 1) with those expressing the density in a state of gas (also referred to H = 1) the astonishing result is seen that the two series are identical.

Elements.	Density. Air = 1	Density. Hydrogen = 1	Atomic Weights.
Hydrogen,	0.0692	1	1
Fluorine,	(1.31)	(19)	19
Chlorine,	2.45	35.45	35.45
Bromine,	5.52	79.96	79.96
Iodine,	8.75	126.86	126.86

From this similarity of the atomic (combination) weights with the densities, follows the cogent conclusion that *in equal volumes of these elementary gases there is contained an equal number of atoms.* Indeed, if in one volume of hydrogen, for example, there are contained 1000 atoms of hydrogen, which equal 1000 weight units, and in a like volume of chlorine there are also present 1000 atoms of chlorine, which equal 1000 × 35.45 weight units, then it is evident that the relation between the atomic weights and that between the densities (the weights of like gas volumes) must be the same.

1 vol. Hydrogen.

1 vol. Chlorine.

These relations can be expressed by the following rule: *The atomic weights of the halogen elements are proportional or equal to their densities,* if referred to the same unit. Yielding to a too hasty generalization, this was incorrectly followed for all elements.

We arrive at a perfectly similar, but much more general conclusion, by the consideration of the physical properties of gases or vapors. The similar deportment of the same under pressure (law of Mariotte and Boyle), their similar expansibility by heat (law of Charles and Dalton, ordinarily the law of Gay-Lussac), only appear comprehensible by the following suppositions. The gases consist of small portions of matter, which are separated by equal distances, very great in proportion to the particles (the distances of the centres are equal and suffer equal alterations). It immediately follows from this, that *equal numbers of particles are contained in equal volumes of all gases* (under like temperature and pressure). The kinetic gas theory, based on the same supposition, explains the similar deportment of gases by the equal kinetic energy of the smallest gaseous particles.

From the proposition, that in equal volumes an equal number of particles are present, it follows directly that their relative weights are proportional to the volume weights or gas densities, and that by the determination of the latter, the first are also given. In what ratio these smallest particles (called molecules) stand to the chemically smallest particles (atoms), remains undetermined, and can only be obtained by a comparison of the volume ratios according to which the bodies combine (p. 73). It is, however, even now seen that, at least in the case of compound bodies, the smallest gas particles must be sums of atoms, as the same consist of combinations of atoms.

It follows, from the equality of the atomic weights and the densities, that the halogens must combine with hydrogen in equal volumes, since 1 part of H by weight combines with 35.45 parts of chlorine by weight, etc., and the weights of equal gas volumes stand in the same ratio. Further: 1 part H and 35.45 parts chlorine yield 36.45 parts HCl; one volume of the latter weighs, however, 18.2 (H = 1, p. 79); consequently, 36.45 parts HCl occupy 2 volumes. Therefore, equal volumes of H and Cl yield a double volume of HCl, or, as ordinarily expressed, 1 volume H and 1 volume Cl yield 2 volumes HCl. In a similar manner it may be deduced that 1 volume H and one volume Br vapor yield 2 volumes of HBr; that 1 volume H and 1 volume I vapor yield 2 volumes of HI.

These conclusions are confirmed by the following experiments:—

1. The concentrated aqueous solution of hydrochloric acid is decomposed by the action of the galvanic current, and the chlorine and hydrogen collected; these gases separate at opposite poles. The electrolysis may be made in an ordinary voltameter (Fig. 46). Hofmann's apparatus is better adapted to this purpose (Fig. 47). Two glass cylinders, provided at the top with stop-cocks, are connected at the lower end with each other and with a funnel tube; the latter serves to fill the apparatus with liquid; and also, by further additions, to press out the gases

collected in the tubes. The platinum electrodes are fused into the lower part of both tubes. In another form of Hofmann's apparatus (Fig. 48) the electrodes are introduced by means of caoutchouc corks. When the separating gases (in this case the chlorine) attack the platinum, carbon electrodes are substituted for the latter.

To electrolyze hydrogen chloride, fill the apparatus with concentrated hydrochloric acid, which is mixed with ten volumes of a saturated salt solution; close the upper cocks, and connect the electrodes with the poles of the battery. Gases separate in both tubes, and in *equal volumes;* that separated at the positive pole may be proved to be chlorine; the other combustible gas is hydrogen.

This experiment shows that hydrogen chloride decomposes into equal volumes of chlorine and hydrogen. The opposite—the production of HCl by the union of equal volumes of H and Cl—is shown in the next experiment.

FIG. 46.

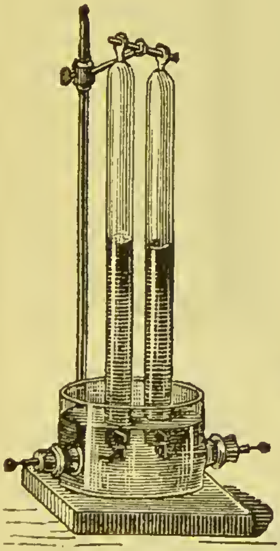
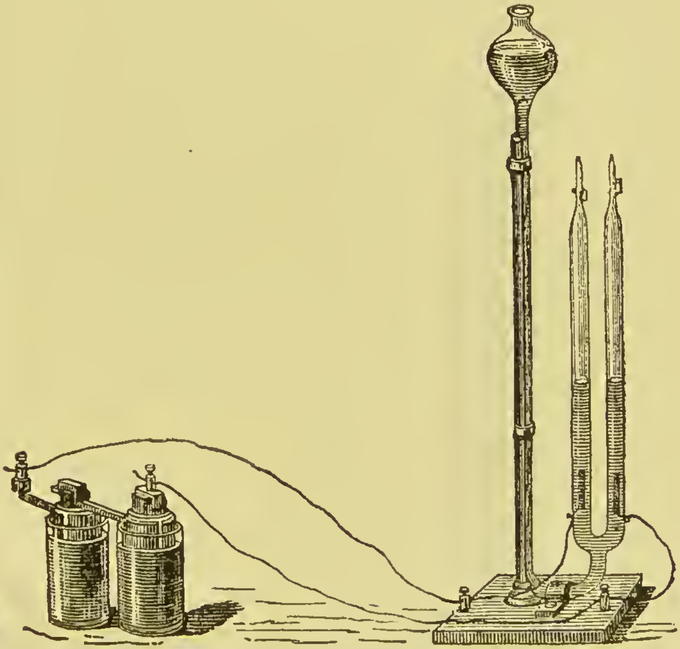


FIG. 47.



2. Fill a cylindrical glass tube, provided with stop-cocks at both ends (Fig. 49), with equal volumes of chlorine and hydrogen. This is most conveniently done by conducting the gaseous mixture obtained by the electrolysis of HCl into the dry tube. (The tube should be filled in the dark, as the gases combine in daylight.) When the tube is filled with the mixture, sunlight or magnesium light is brought to bear upon it, when chemical union ensues. On immersing the lower end of the tube into water, and opening the lower cock, the water will rapidly fill the tube, as the hydrogen chloride that was produced dissolves; all the hydrogen and all the chlorine have disappeared.

3. A modification of this experiment teaches us another important fact which has reference to the ratio of the volume of the hydrogen chloride to the volumes of its constituents. If the tube filled with equal volumes of Cl and H be opened under Hg, after the explosion, no diminution in volume will be detected, although the mixture of Cl and H has been changed to hydrogen chloride. It follows

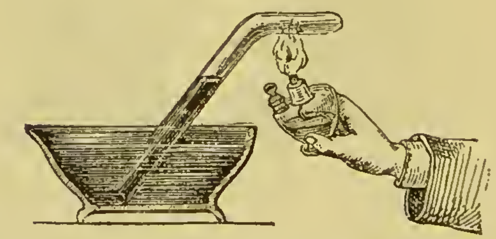
from this that a mixture of equal volumes of Cl and H affords the same volume of HCl, or, as ordinarily expressed, *one volume of Cl and one volume of H yield two volumes of hydrogen chloride.*

The following experiment confirms this conclusion: Into a bent tube (Fig. 50), filled with Hg, conduct dry HCl, and then introduce in the bend of the upper part a little piece of metallic sodium. On heating the latter with a lamp, the HCl is decomposed, the Cl combines with the Na to form sodium chloride, while hydrogen is set free. Upon measuring the residual hydrogen it will be found that its volume is exactly the half of the volume of HCl originally introduced. In the same manner may be shown the fact that in two volumes of HBr and HI there is contained in each one volume of H. It follows further from the densities of bromine and iodine vapors, that the quantities of these elements in gas form combining with one volume of hydrogen also occupy one volume. Hence, *one volume of hydrogen and one volume of bromine vapor yield two volumes of HBr, and one volume of hydrogen and one volume of iodine vapor two volumes of HI.*

FIG. 48.

FIG. 49.

FIG. 50.



The volume ratios in the chemical union of gases were first investigated by Humboldt and Gay-Lussac (1805–1808). The latter derived the two following empirical laws by experiment: (1) Gases unite according to simple volume ratios; (2) The volume of the resulting body bears a simple ratio to the volumes of the constituents.

Comparing this fact announced by Guy-Lussac, that in the chemical union of gases simple volume ratios do occur, with that discovered by Dalton (p. 70), that the quantities by weight of the combining elements also bear a simple ratio, and granting the atomic constitution of matter, it follows that the number of smallest gas particles (molecules) contained in equal volumes of different gases must bear a simple ratio to each other: the *simplest supposition*, however, would be that *this number of molecules in equal volumes of all gases is the same.* These important conclusions were deduced by Avogadro in 1811, and by Ampère in 1814.

As deduced on p. 74, and confirmed by the described experiments, the quantities of the halogen-hydrogen compounds by weight, expressed by the chemical formulas, HCl, HBr, HI, occupy a volume twice as large as one part by weight of H, or 35.45 parts Cl, 79.9 parts bromine, 126.8 parts iodine. While the gas densities of the elements are equal to their atomic weights (p. 73), those of the compound bodies amount consequently to half that expressed by their formulas. From this it would follow that in equal volumes of compound bodies only half as many atoms or particles are present as in an equal volume of an elementary form of matter. In fact, one volume of H, containing *n* atoms of H, combines with one volume of chlorine, which, too, contains *n* atoms of Cl. *n* parts HCl result, which fill two volumes; therefore, there are only $\frac{n}{2}$ parts of HCl contained in one volume of HCl:—

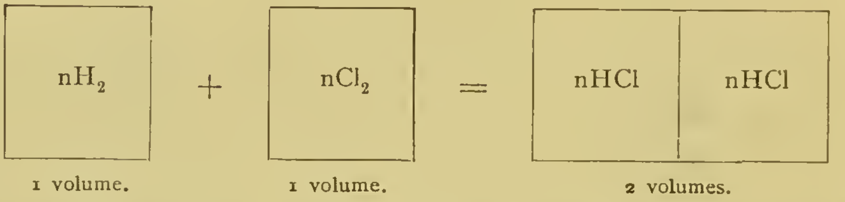
$$\underset{\text{1 vol.}}{\text{nH}} + \underset{\text{1 vol.}}{\text{nCl}} = \underset{\text{2 vols.}}{\text{nHCl.}}$$

This conclusion contradicts the general postulate (p. 74), derived from the physical properties, viz., that *all* gases, both simple and compound, contain the same number of gaseous particles in equal volumes. This contradiction, which for a long time prevented the adoption of the atomic volume theory in chemical science, is now easily solved by the following supposition of Avogadro, announced in 1811. It is necessary to distinguish two different kinds of particles: *molecules* and *atoms*. The smallest discrete particles in gases are not *atoms*, but molecules, which consist of several atoms. That the molecules of compounds consist of atoms, is obvious, since, indeed, the same represent aggregates of atoms; but the elements also form molecules in a free condition, which are composed of several, generally, of *two* atoms. The previously deduced rule (p. 73), that in equal gas volumes of the halogen elements there is contained an equal number of atoms, must be formulated somewhat as follows: *In equal volumes of all gases is found an equal number of molecules* (law of Avogadro).

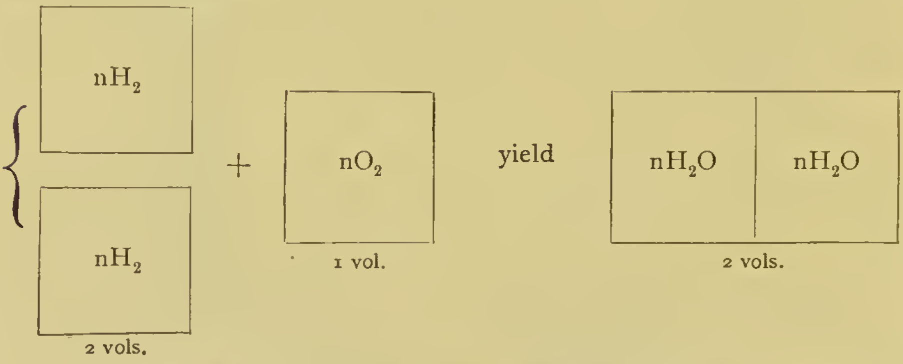
The process of the combination of hydrogen with chlorine (and the other halogens) must be conceived therefore to be somewhat like the following: 1 molecule of H, containing 2 atoms of H, acts upon 1 molecule of Cl, also composed of two atoms of Cl, and there result 2 molecules of HCl:—

$$H_2 + Cl_2 = 2HCl.$$

We can now understand that hydrogen chloride contains just as many molecules in an equal volume as H and Cl. This is apparent from the following representation:—



In a similar manner 2 volumes H (containing 2*n* molecules) give with 1 volume oxygen (containing *n* molecules), 2 volumes aqueous vapor; consequently, 2*n* molecules of water. In 2*n* molecules of the latter (H_2O) there are contained 2*n* atoms of O; therefore in *n* molecules of oxygen, 2*n* atoms of oxygen—or *one oxygen molecule consists of 2 atoms.*



In the same way it may be shown that the nitrogen molecule consists of 2 atoms of nitrogen (N_2), the phosphorus molecule, of 4 atoms of phosphorus (P_4), etc., etc.

This peculiar result, following from the law of Avogadro, that the molecules of the elements consist of several atoms, etc., is shown by many other circumstances founded on facts, for example, by the existence of the allotropic modifications of the elements (compare ozone), by the chemical reactions (compare hydrogen peroxide), and by the remarkable action of the elements in the moment of their liberation.

Upon p. 52 we said that the oxygen separated from water by chlorine acted much more energetically than free oxygen. Other elements, especially hydrogen, behave similarly in the *moment of formation—in statu nascendi.* As viewed by the atomic molecular theory, this may be very easily explained. The free elements (their molecules) are compounds of similar atoms whose chemical affinity has always been partially satisfied. In the moment of their separation from compounds free atoms appear, which, before they combine to molecules, must act more energetically.

All that has been developed in the preceding statements may be summarized in the following sentences: All bodies are composed of elementary atoms. The latter unite to produce the molecules of the simple and compound bodies. Molecules are the smallest discrete particles existing in a free state. The same number of molecules is contained in equal volumes of all gaseous and vapor-forming bodies. Therefore, the gas densities bear the same ratio to each other as the molecular weights. The density is generally compared with that of hydrogen = 1, while the molecular weights are referred to $H_2 = 2$; therefore, the gas densities (the specific gravities of gases) of all bodies are one-half their molecular weights. The atomic weights are compared with H = 1, therefore, the densities of the elements whose molecules consist of two atoms, are equal to the atomic weights:—

Atoms.	Molecules.	Density.
$H = 1.003$	$H_2 = 2$	1.003
$Cl = 35.45$	$Cl_2 = 70.9$	35.45
$Br = 79.9$	$Br_2 = 159.8$	79.9
$I = 126.8$	$I_2 = 253.6$	126.8
	$HCl = 36.45$	18.2
	$HBr = 80.9$	40.45
	$HI = 127.8$	63.9
$O = 16$	$O_2 = 32$	16
	$H_2O = 18$	9
$N = 14.04$	$N_2 = 28.08$	14.04
	$NH_3 = 17.04$	8.52
$P = 31.03$	$P_4 = 124.12$	62.06
	$PH_3 = 34.03$	17.01

A simpler deduction, that the molecules of the elements consist of two or more atoms, is the following: We proceed from the law of Avogadro, that an equal number of molecules is contained in equal volumes of all gases or vapors. This law, or better hypothesis, cannot be proven mathematically, as was attempted; just as little as any other fundamental hypothesis*—but it possesses, as basis of the entire recent kinetic theory of gases, a high degree of probability. It necessarily follows from this law that the molecular weights of all bodies are proportional to the gas densities. Referred to hydrogen as unit, the empirical gas densities of HCl = 18.2, of HBr = 40.4, of HI = 63.9, etc. Analysis shows, however, that 35.4 parts of Cl are in union with 1 part H in HCl, 79.9 bromine in HBr, 126.8 iodine in HI. As the weight of one atom of H is made equal to 1, and 35.4 parts of chlorine are combined with it, the weight of a molecule of hydrogen chloride, consisting of at least one atom of H and one atom of Cl, must equal 36.4; it is, therefore, twice as much as its density, 18.2. Hence the *molecular weights of all other bodies, as they bear the same ratio as the densities, must also be twice as large* (referred to H as unit) *as the latter.* The hydrogen molecule is = 2, and consists of two atoms, as its atomic weight equals 1. The chlorine molecule weighs 70.9 units, and consists of two atoms (Cl_2), if we suppose that the atomic weight = 35.45. Its atomic weight could, however, be only the half (or another submultiple) of 35.4; then its molecule would consist of four chlorine atoms (Cl_4 = 70.9 when Cl is made equal to 17.6), and the formula of hydrogen chloride would be HCl_2. From the densities of the elements in gas form we only ascertain their molecular weights. Their atomic weights are derived from the molecular weights of their compounds, as we regard the *smallest quantity of the element* which analysis discloses *in the molecule of any compound* as the *atomic weight.* Thus, in the molecule of any compound of chlorine there are *never* less than 35.45 parts by weight of Cl. That the maximum values thus derived have not been found too high, but correspond to the actual relative atomic weights, follows from the agreement of these numbers with the atomic numbers obtained from the specific heat of the elements. The complete certainty of their correctness we reach by the law of periodicity, which is formed from these numbers.

Taking one atom of hydrogen as the unit of weight and volume, then two parts by weight of H, or one molecule (H_2), would occupy two volumes. We say, therefore, although incorrectly, that the molecules fill two volumes, and designate the molecular formulas *double volume formulas.* The volume of molecules and atoms is, however, unknown to us; we only know that in equal gas volumes there is contained an equal number of molecules.

These convincing suppositions and conclusions deduced from these actual relations, form the atomic molecular doctrine, which is the foundation of the chemistry of to-day. As this doctrine completely explains the quantitative phenomena arising in the action of the chemical elements upon each other, and as it has been repeatedly confirmed by entirely opposite phenomena, it is only proper and correct that it be designated a theory (p. 71).

OXYGEN GROUP.

In this group are included the elements oxygen, sulphur, selenium, and tellurium. They are perfectly analogous in their chemical deportment. They unite with two atoms of hydrogen.

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* A mathematical proof is only possible upon the basis of another, more general, quantitative hypothesis (or of an axiom), which in turn is not provable.

1. OXYGEN.

$O = 16. \quad O_2 = 32.$

Oxygen (oxygenium) is the most widely distributed element in nature. It is found free in the air; in combination it exists in water. It is an important constituent of most of the mineral and organic substances.

It was discovered, almost simultaneously, by Priestley, in England, 1774, and Scheele, in Sweden, 1775. Lavoisier, in France, 1774–1781, first explained the important rôle attached to oxygen in processes of combustion, of respiration, and of oxidation.

Preparation.—Heat red mercuric oxide, a compound of mercury with oxygen, in a small glass retort; in this way the oxide is decomposed into mercury and gaseous oxygen:—

$$HgO = Hg + O.$$

The following method is commonly pursued in the chemical laboratory: Potassium chlorate, a compound of potassium, chlorine and oxygen, is heated in a glass retort (Fig. 51) or flask, and thus decomposed into solid potassium chloride and oxygen:—

$$KClO_3 = KCl + 3O.^*$$

The evolution of the gas proceeds more regularly and requires a less elevated temperature if the pulverized chlorate be mixed with ferric oxide or manganese peroxide. The liberated oxygen is collected over water.

McLeod (*Jr. Chem. Soc.*, 55, 192) explains the mechanism of the action of manganese peroxide on potassium perchlorate, when heated, as follows: 1st, the peroxide acts on the chlorate producing potassium permanganate, chlorine, and oxygen, $2MnO_2 + 2KClO_3 = K_2Mn_2O_8 + Cl_2 + O_2$. The permanganate is then decomposed by heat: $K_2Mn_2O_8 = K_2MnO_4 + MnO_2 + O_2$, and in the third stage the change is likely: $K_2MnO_4 + Cl_2 = 2KCl + MnO_2 + O_2$.

Very pure oxygen may also be obtained by heating potassium dichromate with sulphuric acid:—

$$K_2Cr_2O_7 + 4H_2SO_4 = Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O + 3O.$$

Besides these, many other methods may be employed for the preparation of the gas: *e. g.*, the ignition of manganese and barium peroxides; the decomposition of sulphuric acid at a high heat; the boiling of a solution of bleaching lime with a cobalt

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[*] The chemical equations used here and previously are only intended to represent the manner of the reaction, and to express the accompanying relative quantities by weight. It should not be forgotten that free atoms do not exist, but that they always occur combined in molecules. Molecularly written the equation would be:—

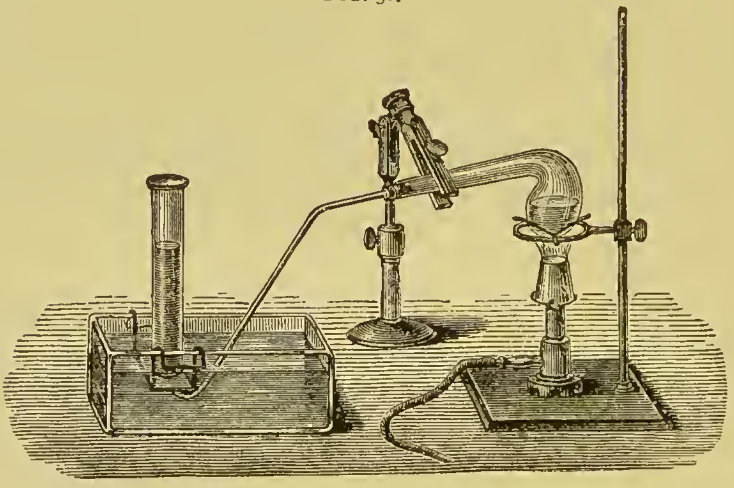
$$2KClO_3 = 2KCl + 3O_2.$$

salt, etc. These methods, applied technically, will be considered more fully later.

A very convenient laboratory method for the preparation of oxygen consists in allowing dilute hydrochloric acid to act upon a mixture of barium peroxide (2 parts) and manganese peroxide (1 part). The gas is evolved at the ordinary temperatures. If the solid ingredients are mixed with gypsum and a little water the mass can be moulded into cubes, and the oxygen then be generated in a Kipp apparatus (*Berichte*, 20, 1585).

Properties.—Oxygen is a colorless, odorless, tasteless gas. Its density equals 16 (H = 1.003), or 1.1060 (air = 1). One litre of oxygen at 0°C., and 760 mm. pressure, weighs 1.4330 grams (16 times more than one litre of hydrogen). It is only slightly soluble in water; 100 volumes of the latter dissolve 4.1 volumes of the gas at 0°, and 2.9 volumes at 15°. It is more readily dissolved by absolute alcohol (28 volumes in 100 volumes).

FIG. 51.



The critical temperature of oxygen is —118°, and its critical pressure equals 50 atmospheres (p. 48). Liquid oxygen under a pressure of 1 atmosphere boils at —181°, and under 9 mm. pressure at —225°. Its specific gravity at —118° equals 0.65, at —139° it is 0.87, and 1.124 at —181°.

Oxygen combines with all the elements excepting fluorine. With most of them it unites directly, accompanied by the evolution of light and heat. The combustion of bodies which burn in the air depends on their union with oxygen, which is present in the same to the amount of 23 per cent. The phenomena of the respiration of animals are also influenced by the contact of the oxygen of the air—hence the earlier designations of oxygen as inflammable air, and vital air. In pure oxygen the phenomena of combustion proceed more energetically. Ignited charcoal or an ignited sliver inflames immediately in the gas, and burns with a bright light. This test serves for the recognition of pure oxygen. Sulphur and phosphorus ignited in the air burn in it with an intense light (Fig. 52). Even iron is able to burn in the gas. To execute this experiment, take a steel watch spring, previously ignited, attach a match to the end, ignite the same, and then introduce the spring into a vessel filled with oxygen gas (Fig. 53). At once the match inflames and ignites the iron, which burns with an exceedingly intense light and emits sparks. (To protect the vessel from the fusing globules of iron oxide, cover the bottom with a layer of sand.) Iron will burn in any flame if a current of oxygen be conducted into the same.

FIG. 52.

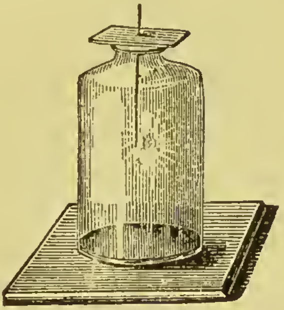
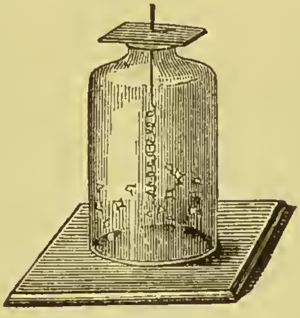
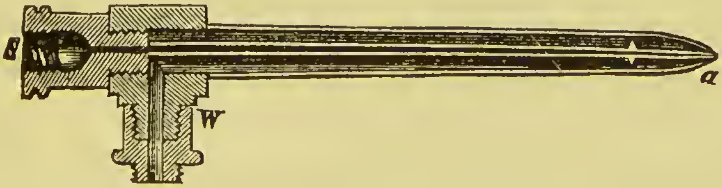


FIG. 53.



Oxygen combines with hydrogen to form water. The union occurs at a red heat, by the electric spark or by the action of platinum sponge (p. 45). Hydrogen burns in oxygen with a flame; *vice versa,* oxygen must also burn in hydrogen; this may be demonstrated in the same manner as indicated under hydrogen chloride (p. 56). A mixture of hydrogen and oxygen detonates violently; most strongly if the proportions are 1 volume of oxygen and 2 volumes of hydrogen; such a mixture is known as oxy-hydrogen gas. The explosibility may be shown in a harmless way by the following experiment: Fill a narrow-necked flask of 4-6 ounces, over water, ⅔ with hydrogen, and ⅓ oxygen; close the opening with a cork, then wrap the flask up in a towel, remove the cork and bring a flame near the opening. A violent explosion ensues, generally with complete breaking of the flask.

FIG. 54.



The oxy-hydrogen flame is only faintly luminous; it possesses, however, a very high temperature, answering, therefore, for the melting of substances which fuse with great difficulty, *e. g.*, platinum. To get a continuous oxy-hydrogen flame, efflux tubes of peculiar construction are employed (Fig. 54); through the outer tube, *W*, hydrogen is brought from a gasometer; oxygen is conveyed through the inner *S*, and the mixture ignited at *a*. Such a flame impinging on a piece of burnt lime makes the latter glow and emit an extremely bright light—*Drummond's Lime Light.*

The union of oxygen with other substances, is termed *oxidation.* This term, as well as the name oxygenium (from ὀξύς and γεννάω), or acid producer, arises from the fact that acids are sometimes formed in oxidation. This the combustion experiments, previously mentioned, prove. If the vessels, for instance, in which carbon, sulphur, and phosphorus were burned, be shaken up with water, the latter will give an acid taste, and redden blue litmus paper. It was formerly thought that the formation of acids is always conditioned by oxygen. We have, however, already noticed that the haloid acids HCl, HBr, and HI, contain no oxygen. Some of the elements yield acids by their union with oxygen, or more correctly *oxides*, which form *acids* with water. Most of these are the metalloids. Thus the following corresponding acids are derived from the acid-forming oxides of sulphur and phosphorus:—

$$\underset{\text{Sulphur trioxide.}}{SO_3} + H_2O = \underset{\text{Sulphuric acid.}}{H_2SO_4}$$

$$\underset{\text{Phosphorus pentoxide.}}{P_2O_5} + H_2O = \underset{\text{Metaphosphoric acid.}}{2HPO_3}$$

With oxygen the metals usually yield oxides, which form *hydroxides* (hydrates) or *bases* with water:—

$$\underset{\text{Pot. oxide.}}{K_2O} + H_2O = \underset{\text{Potas. hydroxide.}}{2KOH}$$

$$\underset{\text{Calcium oxide.}}{CaO} + H_2O = \underset{\text{Calc. hydroxide.}}{Ca\,(OH)_2}$$

The salts are produced by the alternating action of acids and bases (see p. 60).

Thirdly, there exist the so-called *indifferent oxides*, which yield neither acids nor bases, with water, *e. g.*,

$$\underset{\text{Nitrous oxide.}}{N_2O} \qquad \underset{\text{Nitric oxide.}}{NO} \qquad \underset{\text{Barium peroxide.}}{BaO_2}$$

Oxidation is not only induced by free oxygen or bodies rich in it, but frequently, also, by the halogens; in the latter case the halogens first decompose the water with the elimination of oxygen, which then oxidizes further (compare p. 52).

The opposite of oxidation, the removal of oxygen, is called *reduction*. Hydrogen (in statu nascendi), and substances giving it off easily (as HI), have a reducing action. Most of the metallic oxides are reduced at a red heat, by hydrogen, *e.g.* :—

$$\underset{\text{Copper oxide.}}{CuO} + H_2 = \underset{\text{Copper.}}{Cu} + H_2O.$$

OZONE, O_3.

Ozone, discovered in 1840, by Schönbein, is a peculiar modification of oxygen, characterized by a remarkable odor and great ability to react, therefore it is called *active oxygen*. It is obtained from oxygen in various ways; it is almost always produced when this gas is liberated, or when it takes part in a reaction; thus, in the decomposition of peroxides by concentrated sulphuric acid, in the electrolysis of water (at the positive pole), in the slow oxidation of moist phosphorus, in the combustion of hydrocarbons, and in the action of the so-called silent discharge in an atmosphere of oxygen or air. In none of these instances is all the oxygen ever converted into ozone; only a small portion—in most favorable conditions 5–6 per cent.—suffers this change.

The following methods serve for the preparation of ozone:—

1. Bring several pieces of stick phosphorus into a spacious flask, cover them about half with water, and allow them to stand for some hours. Or conduct oxygen over pieces of phosphorus placed in a glass tube and moistened with water. Ozone is also formed abundantly when a potassium bichromate solution is substituted for water.

2. Pass the electric spark from an electrical machine or a Ruhmkorff coil through air or oxygen. The silent discharge from a powerful induction current is better. For this purpose we can employ a Siemen's induction tube (Fig. 55), which consists of a glass tube covered without with tin foil, in the interior of which is a smaller tube coated upon its inner side. The oxygen circulates between the two tubes; the two coatings are in connection with the induction spiral, or the poles of a Holtz electrical machine. The Berthelot induction tube is well adapted for ozonization. In it dilute sulphuric acid replaces the metallic coatings.

3. Gradually add barium peroxide in small portions (or potassium permanganate) to cold sulphuric acid:—

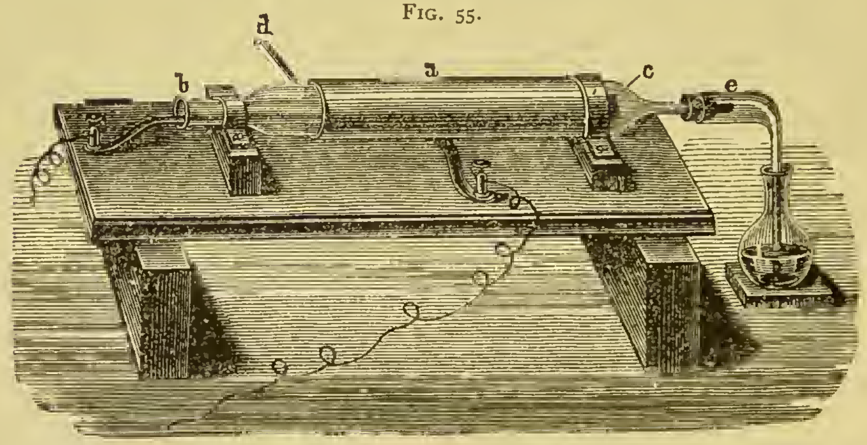
$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O + O.$$

The escaping oxygen is tolerably rich in ozone, and is collected over water.

Ozone possesses a highly penetrating, chlorine-like odor (phosphorus odor), which by prolonged respiration produces bad results. In a long layer, ozone shows a bluish color. If ozonized air be subjected to powerful pressure (150 atmospheres) at a very low temperature, or if ozonized oxygen be conducted through a small tube cooled to —181° by boiling oxygen, the ozone will condense to a liquid with an indigo-blue color. Liquid ozone, if preserved in a sealed tube, passes into a blue gas, that can be again liquefied by chilling it with boiling ethylene. Ozone is rather stable at the ordinary temperature; when heated to 300° C., it reverts to ordinary oxygen. It is somewhat soluble in pure water; the larger portion of it is, however, converted by the water into oxygen, without formation of hydrogen peroxide. Unlike ordinary oxygen, ozone, especially in a moist state, oxidizes strongly at ordinary temperatures. Phosphorus, sulphur, and arsenic are converted into phosphoric, sulphuric, and arsenic acids; ammonia is changed to nitrous and nitric acids; silver and lead are converted into the corresponding peroxides; therefore paper moistened with a lead salt is colored brown. Iodine is separated from potassium iodide by it:—

$$2KI + H_2O + O = 2KOH + I_2.$$

FIG. 55.



It also oxidizes all organic substances, like caoutchouc; therefore the apparatus used in its preparation must not be constructed of the latter. Solutions of dye stuffs, like indigo and litmus, are decolorized. Very characteristic for ozone is its ability to turn an alcoholic solution of guaiacum tincture blue.

Liquid ozone boils at — 106°. If it be enclosed in a glass tube it changes to a blue gas, which may be recondensed by cooling it by means of boiling ethylene.

For the detection of ozone the ordinary potassium iodide starch paper (Schönbein) may be used. This is prepared by immersing white tissue paper in a starch solution mixed with potassium iodide. The iodine which the ozone liberates from the potassium iodide blues the starch paper. The quantity of ozone may be approximately determined from the rapidity and the intensity of the coloration; the reactive power is, however, very much influenced by aqueous vapor. Thallous hydroxide is a more reliable reagent for ozone than the potassium iodide paper. Guaiacum tincture and paper saturated with a lead acetate solution may also be used to detect ozone; the first acquires a blue color, the second is browned. Other substances also blue potassium iodized starch and guaiacum, *e. g.*, chlorine, bromine, nitrogen dioxide, etc., etc. To distinguish ozone from these, proceed as follows (Houzeau): Take two strips of violet litmus paper, one of which is saturated with KI, and expose it to the action of the gas; when O_3 is present potassium hydroxide will be formed from the KI, and color the violet litmus blue. The second paper serves to show the absence of ammonia.

The preceding reactions of ozone are all produced by hydrogen peroxide, although less rapidly. The only test answering for the distinction of very slight quantities of ozone from hydrogen peroxide, is the blackening of a bright strip of silver by ozone.

Ozone is formed from pure oxygen, and is nothing more than the latter condensed. The molecules consist of 3 atoms of O:—

$$\underset{\text{3 vols. oxygen.}}{3O_2} \quad \text{yield} \quad \underset{\text{2 vols. ozone.}}{2O_3}.$$

This is proved by the following experiments: In ozonizing oxygen its volume diminishes; upon heating (whereby ozone is again changed to oxygen), the original volume is reproduced; when ozonized oxygen is brought in contact with oil of turpentine or cinnamon, all the ozone is absorbed and the volume of the gas is diminished. Comparing this diminution, corresponding to the ozone volume, with the expansion which an equal volume of ozonized oxygen suffers after the application of heat, we will find that the first is twice as large as the latter; this indicates that 1 volume of ozone yields 1½ volumes of oxygen. From this it follows that the specific gravity of ozone must be 1½ times greater than that of ordinary oxygen, and that if the molecule of O consists of 2 atoms, the molecule of ozone must contain 3 atoms. This conclusion is confirmed by the specific gravity of ozone derived experimentally from the velocity of diffusion. The density of ozone is found to be 24 ($H = 1$); the molecular weight of it, therefore, is $24 \times 2 = 48$, a number almost equal to the trebled atomic weight of oxygen ($3 \times 16 = 48$). The molecular formula of ozone is, therefore, O_3.

A diminution in the volume of the gas does not occur in the action of ozone upon oxidizable bodies like KI and Hg, although all the ozone disappears. It would appear from this, that in oxidizing, ozone only acts with one atom of oxygen, which occupies the same volume as the ozone:—

$$\underset{\text{1 vol.}}{O_3} + 2KI = \underset{\text{1 vol.}}{O_2} + K_2O + I_2.$$

As a consequence of this behavior, ozone is also called oxidized oxygen; *i. e.*, free oxygen (O_2), which has combined with an additional oxygen atom.

Thermo-chemical Deportment.—Compared with ordinary oxygen, ozone is an endothermic compound. Heat is absorbed in its formation from oxygen (p. 28):

$$(O_2,O) = O_3 \quad . \quad . \quad . \quad . \quad (-32.4 \text{ Cal.})$$

This explains why ozone is produced with so much difficulty, and why the addition of considerable energy is necessary. This may be applied directly in the form of heat or electricity (electric sparks, silent electric discharge), or it may be withdrawn from the heat of formation of other exothermic compounds which are produced at the same time, *e. g.*, the formation of ozone by the oxidation of phosphorus to phosphorous acid.

Being an endothermic derivative, we readily perceive why ozone is so unstable. It reverts to oxygen with the separation of the excessive energy. Herein is manifest the cause of the greater reactivity of ozone as compared with oxygen. All oxidations performed by ozone are more energetic, because there are 32.4 Cal. more set free in them than in oxidations with ordinary oxygen.

We observe, therefore, that the elementary substance oxygen occurs in free condition in two different forms—*allotropic modifications*—ordinary oxygen (O_2) and ozone (O_3). We will learn later that very frequently substances of the same elementary composition possess different physical and chemical properties; such bodies are called *isomerides* and the phenomenon *isomerism.* The isomerism of the elements is known as *allotropy;* this is accounted for (as in the case of oxygen and sulphur) by the different number of atoms in the molecule.

The phenomena of isomerism constitute an important argument for the atomic constitution of matter. If in the chemical union of two bodies the particles of matter would entirely permeate and blend into each other, the existence of isomeric bodies would scarcely be comprehensible. We can therefore only suppose a co-stratification of the atoms, and must consider isomerism as only a varied arrangement of the same. Special allotropy verifies the conclusion drawn from the gas density that the molecules of the elements are composed of atoms.

We have already seen that ozone is absorbed, not only by turpentine and cinnamon oil, but also by other ethereal oils. These bodies are, however, only very slowly oxidized; the ozone is contained in them in a peculiar, combined condition. In this form it acts upon some bodies like free ozone; in other instances, the oxidizing action is only rendered possible by peculiar substances which carry the ozone. Spongy platinum, ferrous sulphate, and the blood corpuscles are examples of this class. Thus, old turpentine oil, containing absorbed ozone, only acts on paper saturated with starch and potassium iodide, if a few drops of a ferrous sulphate solution have been added to it.

Since ozone is formed when electricity acts upon air, and, indeed, probably, in all oxidation and combustion processes; and, further, potassium iodide starch paper is blued when exposed to the air; it was believed that ozone was a constant constituent of atmospheric air (1–10 milligrams in 100 litres of air); according to recent investigations it is, however, probable that the imagined ozone reactions are frequently produced by hydrogen peroxide, which is very similar to ozone in reaction (p. 87), and is almost constantly in the air (Schöne).

Antozone, which was regarded as a third peculiar modification of oxygen, has been proved to be hydrogen peroxide.

COMPOUNDS OF OXYGEN WITH HYDROGEN.

1. WATER.

$H_2O = 18$. Density $= 9$.

Water, the product of the union of hydrogen with oxygen (p. 83), is produced in many chemical processes, *e. g.*, in the formation of salts from bases and acids (p. 60).

Cavendish was the first (1781) to confirm the formation of water by the combustion of hydrogen. Lavoisier first (1783) determined its quantitative composition. Later (1805) Gay-Lussac showed that it was produced by the union of two volumes of hydrogen with one volume of oxygen.

Physical Properties.—It is obtained chemically pure by the distillation of naturally occurring water, which always contains other matter dissolved in it. It appears in all three states of aggregation; in the liquid, gaseous (steam), and solid (ice, snow). When water is cooled it contracts and attains its greatest density at + 3.7° C., the maximum contraction. The weight of a cubic centimeter of such water is taken as the unit of weight (= 1 gram). By further cooling the water expands—the opposite of most other bodies; its volume becomes greater, while the specific gravity decreases.

The following table gives the volume and specific gravity of water for different temperatures (according to Kopp):—

Temperature.	Volume.	Specific Gravity.
0°	1.00012	0.99988
2°	1.00003	0.99997
4°	1.00000	1.00000
6°	1.00003	0.99997
8°	1.00011	0.99989
10°	1.00025	0.99975
12°	1.00044	0.99956
14°	1.00068	0.99932
16°	1.00097	0.99903
18°	1.00131	0.99869
20°	1.00169	0.99831
22°	1.00212	0.99789
24°	1.00259	0.99742

By cooling water solidifies to ice. The solidification-temperature of water, or more correctly the fusing point of ice, is taken as the zero of Celsius's and Réaumur's thermometric scales. We can, however, reduce still water considerably below the 0° point without its freezing, while the *fusing point* of ice, like all other solid bodies, is *constant* (at a definite pressure).

In the conversion of water into ice, a considerable expansion occurs: 100 vols. H_2O at 0° yield 107 vols. ice at 0°; the specific gravity of the latter is, therefore, 0.93. Ice crystallizes in hexagonal forms, as may be distinctly observed in snow-flakes.

Different bodies require different quantities of heat to bring them to the same temperature. The heat capacity of water is greater than that of all other liquid or solid bodies. It is customary to take the quantity of heat necessary to raise one part by weight of H_2O from 0° C., to 1° C., as the unit of heat, or calorie. In the passage of a liquid to the solid state heat is always set free, while, on the other hand, in the fusion of the solid heat is absorbed. The *latent* heat of water equals 79 calories; that means, that for the fusion of one part of ice by weight, a quantity of heat is required which is capable of raising one part H_2O from 0° to 79° C.

Water boils upon the application of heat, and is converted into *steam*. The boiling temperature, like that of all other liquids, depends on the pressure; it is also influenced by the substances dissolved in it, although the temperature of the vapors is constant (at a given pressure). The temperature of the steam escaping from water at the ordinary pressure of 760 mm. is = 100° of the thermometric scale of Celsius (= 80° Réaumur).

One volume of water, at 100° C., yields 1696 volumes of vapor of the same temperature. The specific gravity of steam $= \frac{18}{2} = 9$ (H = 1), or $\frac{9}{14.48} = 0.623$ (air = 1). One litre of aqueous vapor weighs 0.8064 grams (at 0°).

The critical temperature of water (or its absolute boiling temperature, p. 47) is + 370°, and its critical pressure 195.5 atmospheres, *i. e.*, at 370° the tension of its vapor equals 195.5 atmospheres, and above this temperature it can no longer exist as a liquid.

The vaporization of water, and of other liquids, occurs not only at the boiling point, but also at lower temperatures. The tension of the vapors is measured by the height of the mercurial column, which holds it *in equilibrio*.

The following table gives the tension of aqueous vapor for various temperatures:—

Temperature.	Tension.	Temperature.	Tension.
—20° C.	0.93 mm.	40° C.	54.9 mm.
—10° C.	2.15 mm.	60° C.	148.9 mm.
0° C.	4.6 mm.	80° C.	354.3 mm.
+10° C.	9.1 mm.	100° C.	760.0 mm.
20° C.	17.4 mm.	120° C.	1491.0 mm.

Moist gases, therefore, occupy a larger volume than those which are dry. The above table will answer to reduce the observed volume of a moist gas to its volume when dry, by deducting from the observed atmospheric pressure the tension of steam (in mm.) corresponding to the given temperature. (Compare p. 123.)

A definite quantity of heat, requisite for the conversion of a liquid into a vapor, is applied to internal and external work; therefore, it disappears as heat, or becomes latent. The latent heat of the evaporation of water equals 536.5 heat units at 100° C.; *i. e.*, for the conversion of one part of water of 100° C., into vapor of the same temperature, a quantity of heat will be absorbed capable of raising 536.5 parts of H_2O from 0° to 1°.

In consequence of the evaporation of water, the gases separating from an aqueous solution are always moist. To dry the same, conduct them over such substances as will be able to take up the moisture, *e. g.*, calcium chloride, stick potash, sulphuric acid, phosphorus anhydride (compare page 42). Many solids abstract moisture from the air without chemically uniting with it; to dry these let them stand in an enclosed space over sulphuric acid (dessicators).

The Natural Waters.—As water dissolves many solid, liquid, and gaseous compounds, all naturally occurring waters contain foreign admixtures. The purest natural water is rain and snow water; it contains upward of 3 per cent. by volume of gases (oxygen, nitrogen, and carbon dioxide), and traces of solids (the ammonium salts of nitrous and nitric acids). If water that has been standing exposed to the air be heated, the dissolved gases escape in bubbles.

River and spring waters contain, on an average, from 1 to 20 parts of solid constituents in 10,000 parts. Water having much lime and gypsum present in it, is ordinarily known as *hard*, in distinction from *soft* water, which contains less lime (see Calcium Carbonate). On boiling lime waters, most of the impurity deposits out. Spring water generally contains in addition larger quantities of carbon dioxide, which impart a refreshing and enlivening taste to it. Spring waters holding considerable quantities of solid constituents, or exhibiting special healing properties, are called *mineral waters*. These are distinguished as saline waters (containing sodium chloride), sulphur waters (hydrogen sulphide), acidulated waters (saturated with carbon dioxide), chalybeate waters (containing iron), and others.

Sea water contains 3.5 per cent. of salts, of which 2.7 per cent. are sodium chloride.

To purify the natural waters they are filtered (for the removal of mechanical admixtures), and for chemical purposes, distilled (*distilled water*) in apparatus of varying form.

Solutions.—The phenomena appearing in the dissolving of substances indicate that solutions are not mere mechanical mixtures. In every solution alterations occur in the temperature of the liquid. The solubility of solid and liquid substances increases usually with the temperature, while that of gases diminishes. The quantity of dissolved gas is frequently proportional to the pressure; other gases, on the contrary, which are readily soluble in water, such as the halogen-hydrogen compounds, are exceptions to this rule. Heat does not completely expel them from their solutions; they distil over as liquids of definite composition (compare pp. 59 and 65). When they dissolve, a large quantity of heat is liberated, just as in the case of chemical compounds. Further, a contraction is always perceived in the solution of solids and liquids; the volume of the solution is less than the sum of the volumes of the constituents. These phenomena point to the acceptance of a certain affinity between the dissolving bodies. Therefore, solutions, like *alloys*, are designated *undetermined compounds*, in contrast to the *determined compounds*, which are combined according to constant atomic weight ratios. This view is also confirmed by the fact that frequently definite compounds containing water do exist in solution. Such compounds often separate, unaltered, when their solutions are evaporated; the water present in them is known as *water of crystallization*. It is, however, impossible to draw a sharp line between determined and undetermined compounds, between chemical and physical attraction.

THERMO-CHEMICAL DEPORTMENT OF SOLUTIONS.

When a substance is dissolved in water there occurs a change of energy, just as in chemical transpositions; heat is either liberated or absorbed. Solids are also liquefied in their solution; for this a definite quantity of heat (latent heat of fusion, p. 91) is requisite. This is derived from the solvent. Consequently the solution of solids is invariably accompanied with heat absorption, which is evident from the following heats of formation of the halogen derivatives of potassium:—

$$(KCl, Aq.) = -4.4; \ (KBr, Aq.) = -5.08; \ (KI, Aq.) = -5.1.$$

Heat is only disengaged, if the solid happens to unite chemically with the solvent (to form a hydrate)—when the heat of combination exceeds the heat of solution of the hydrate. Gases, on the contrary, which are also liquefied when dissolved, throw off their latent heat of evaporation (p. 91), and therefore dissolve with heat disengagement. The quantity set free, however, is inconsiderable. The great heat disengagement in the solution of the halogen hydrides in water,

$$(HCl, Aq.) = 17.3; \ (HBr, Aq.) = 19.9; \ (HI, Aq.) = 19.2,$$

is due to the formation of the hydrates $HCl + 8H_2O$, $HBr + 5H_2O$, etc., which distil off unaltered (p. 63).

The heat liberated in these solutions exerts a great influence upon the course pursued by chemical reactions, inasmuch as the transpositions often proceed quite differently in the presence of water from that taken when the latter is absent. This is in accord with the principle of the greatest development of heat. This has already been quite fully discussed under the action of oxygen upon the halogen hydrides (p. 68). The heat of solution manifests itself in a similar manner in the action of iodine upon hydrogen sulphide (p. 69).

Chemical Properties of Water.—Water is a neutral substance, *i.e.*, it possesses neither acid nor basic properties. As we have already observed (p. 84), it forms bases with basic oxides and acids with acid-forming oxides.

Despite the fact that the affinity of hydrogen for oxygen is so great, water may, however, be decomposed by many substances. At ordinary temperatures, metals like K, Na, and Ca, decompose it, with liberation of hydrogen:—

$$2H_2O + K_2 = 2KOH + H_2.$$

Other metals do not decompose it, except at elevated temperatures. Steam conducted over ignited iron gives its oxygen to the latter, forming ferroso-ferric oxide, while hydrogen is set free:—

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

Chlorine decomposes water in the sunlight; the decomposition is more rapid when the vapors are conducted through heated tubes:—

$$H_2O + Cl_2 = 2HCl + O.$$

Electrolysis of Water.—The electric current, acting upon water acidulated with sulphuric acid, decomposes the former into its elements. Hydrogen collects upon the negative pole—the *cathode*, while oxygen appears at the positive pole—*the anode.* The volume of the hydrogen is nearly twice that of the oxygen (p. 100).

The electrolytic decomposition of water is more complex than is ordinarily supposed, as perfectly pure water is not capable of conducting the current, and is consequently not decomposed by it. It is rather the added sulphuric acid which suffers the decomposition. Hydrogen and oxygen are merely the end products of this change (see Electrolysis of Salts). In addition to oxygen, about one per cent. of ozone is also produced; further, sulphur heptoxide and hydrogen peroxide are formed at the anode. Some hydrogen peroxide is also produced at the negative pole, as the result of the union of nascent hydrogen with the dissolved oxygen.

Thermo-chemical Deportment.—Water is a strongly exothermic compound, and is formed from its elements with the liberation of much heat. 57.2 Cal. are disengaged in the union of 2 grams of hydrogen with 16 grams of oxygen to produce aqueous vapor of 100° (H_2,O—vapor). In the condensation of the steam to water of 100° 9.63 Cal. are liberated ($= 18 \times 0.536$); this is the latent heat of evaporation (see p. 91). And again, in the cooling of the water through every 1° C., $\frac{18}{1000}$ Cal. more escape—so that in the production of the molecular weight (18 gr.) of water of 16° temperature from its elements, there is a total disengagement of 68.3 great calories (p. 66):—

$$(H_2,O - \text{vapor}) = 57.2 \text{ Cal.} \quad (H_2,O - \text{liquid}) = 68.3 \text{ Cal.}$$

As a consequence of this great heat disengagement, we find water to be a very stable derivative. If we desire to effect its decomposition, we must return to it all the energy that has been withdrawn. Its decomposition by heat (dissociation) does not begin until near 1000°, and it is half finished at 2500° (see below). The entire chemical behavior of water is accounted for by its thermal value; this may also be remarked of its deportment toward the halogens, and of oxygen with reference to the halogen hydrides (p. 68). Upon comparing the heat of formation of the metallic oxides and hydroxides, we obtain a more striking evidence of the behavior of water toward metals, to which we will have frequent occasion to refer in the subsequent groups. If, in agreement with the following equation:—

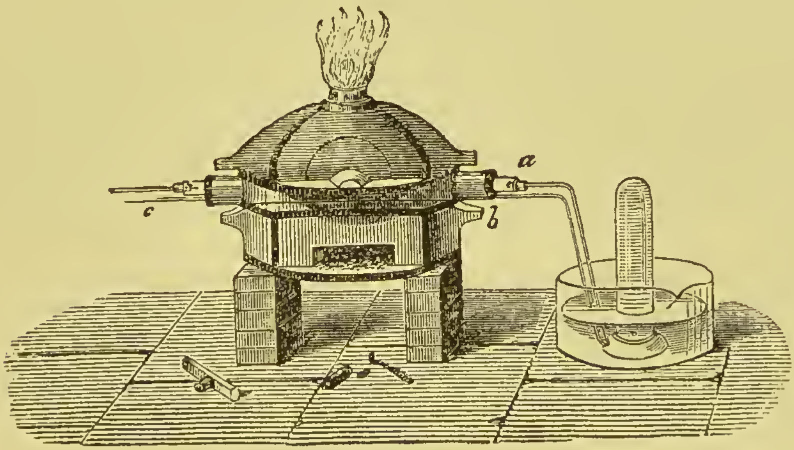
$$H_2O + 2Me = MeO + H_2, \text{ or}$$
$$H_2O + Me = MeOH + H,$$

we discover the heat of formation of the metallic oxides and hydroxides to be greater than that of the water, the latter will be decomposed, and the energy with which this will occur will be greater, the greater the excess of the thermal value. When the heat of formation is less than that of water, the oxides will be reduced by hydrogen with production of water.

Dissociation of Water.—Water, like other chemical compounds, is broken up into its elements by heat. This was first observed upon pouring molten platinum into water, when bubbles of oxy-hydrogen gas appeared (Grove). This decomposition of water was first ascribed to a catalytic action of the platinum. Sainté-Claire Deville was the first to carefully investigate and explain the decomposition phenomena, thus disclosing one of the most important chapters of theoretical chemistry. He proved that a decomposition—dissociation—like the preceding did not take place suddenly, but gradually; that it advanced regularly with increasing temperature, and was limited by an opposing combination-tendency on the part of the components. The temperature at which the decomposition is half finished, is usually designated as the temperature of decomposition.

The following experiment illustrates this: Pass aqueous vapor through a porous clay tube, *a*, puttied into a wider non-permeable porcelain tube heated to a white heat in an oven (Fig. 56). The water suffers partial decomposition, the lighter hydrogen, which passes through into the porcelain tube more rapidly than the oxygen, escapes through the gas tube *b*. The oxygen escapes mainly through the inner tube at *a*. A part of the same diffuses simultaneously with the hydrogen and reunites with the latter. To avoid this, conduct a stream of carbon dioxide through the wider porcelain tube; this will carry out the hydrogen with it. The carbon dioxide will be absorbed by the alkali solution in the collecting vessel, and oxy-hydrogen gas be found in the cylinder. The decomposition of the water commences about 1000°, and is half finished about 2500°. The quantity of gas liberated in equal times rises successively with the temperature.

Fig. 56.



Many other compounds, as carbon dioxide, hydrogen chloride, iodine (p. 54), ozone, ammonium chloride, phosphorus pentachlor-

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* A tube of platinum may be well substituted for the porous porcelain tube; at a red heat it permits the passage of hydrogen, but not that of oxygen.

ide, etc., are similarly dissociated by heat. They are all exothermic compounds, absorbing energy in their decomposition, and are therefore decomposed but gradually, depending upon the amount of energy imparted to them. In these instances heat opposes the affinity of the various components, so that if the temperature be lowered there will occur a partial reunion of the same. The splitting up of the endothermic compounds is entirely different, *e. g.*, that of potassium chlorate, $KClO_3$, into potassium chloride and oxygen, of ammonium nitrite, NO_2 NH_4, into water and nitrogen, of nitrogen chloride into chlorine and nitrogen, etc. Heat is set free in the decomposition of these compounds. Any added or external heat only incites or brings on the decomposition and overcomes the chemical affinity. Under some conditions there are accompanying explosions; there is no reunion of the components on lowering the temperature.

The explanation of the *dissociation* phenomena is found in the kinetic theory of gases and heat. According to it, not only the gas molecules have a direct oscillating movement, inasmuch as they rebound from each other, like elastic balls, but even the atoms in the molecule possess heat vibrations. The velocity of the oscillations of molecules and atoms increases with augmented temperature; it is, therefore, understood that by a determined energy of the oscillations the chemical affinity is overcome and the united atoms are separated from each other. Further, as a consequence of irregular collision, the molecules do not all possess the same velocity at a given temperature; some move more rapidly, others slower; the former are warmer than the latter. Only the sum of the existing forces of all the molecules is a constant quantity at every temperature. The more highly heated molecules, whose number increases with the temperature, yield, therefore, to the decomposition. From this we discover that the dissociation is gradual and increases with the temperature. The law of dissociation is expressed by the curve of probability.

The dissociation of solids, which when heated develop gaseous ingredients, is very instructive and remarkable—for example, the decomposition of calcium carbonate, $CaCO_3$, into calcium oxide and carbon dioxide, of sodium and potassium hydrides into their elements, etc. These indicate that the dissociation is not only dependent upon the temperature but also upon external pressure, and that for every temperature there is a corresponding definite tension of dissociation—a pressure below which the decomposition will not occur. For further particulars on this point see potassium hydride and calcium carbonate.

Dissociation, *i. e.*, the partial decomposition, increasing with the temperature, explains many chemical processes and phenomena. Thus it accounts for the abnormal vapor densities, which apparently contradicted the law of Avogadro (p. 77); all variations from it are always due to the breaking up of more complex molecules (see sulphur, p. 107). Conversely, the observed vapor density affords a clue to the magnitude of the dissociation. The mass action in inverse chemical reactions is afforded a simple explanation by dissociation. We have already said that iron raised to a red heat decomposed water with the separation of hydrogen and the production of ferrous-ferric oxide :—

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

On conducting H over ignited iron oxides the opposite process occurs ; the oxygen compound of the iron is reduced and water and iron are formed :—

$$Fe_3O_4 + 4H_2 = 3Fe + 4H_2O.$$

In the first instanee the excess of water acts. Some of its molecules are dissociated; oxygen combines with iron, while the liberated H is carried away by the excess of steam. In the second case, we can suppose that some of the hydrogen molecules are dissociated, the free hydrogen atoms withdraw oxygen from the iron oxide and form water with it, which is removed by the excess of hydrogen, and thus prevented from acting on the reduced iron. In the action of the bodies in an enclosed space at a given temperature there must occur a state of equilibrium, in which Fe_3O_4, Fe, H_2O and H_2 occur simultaneously. Such a state occurs in every dissociation.

Similarly, hydrogen chloride is decomposed at a red heat by oxygen with the formation of steam and chlorine gas, while in turn steam and chlorine gas are transposed into hydrogen chloride and oxygen (p. 68). As hydrogen chloride is more stable than water and only dissociated at high temperatures, its formation is the predominating process at a red heat.

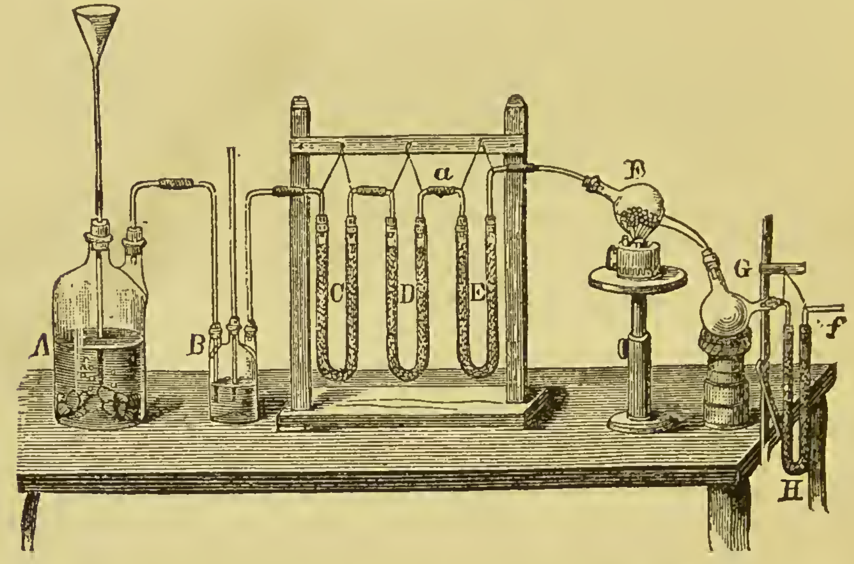
THE QUANTITATIVE COMPOSITION OF WATER.

The composition of water by weight is best determined by a synthesis of the same ; this may be done by reducing cupric oxide with hydrogen :—

$$\underset{\text{Cupric oxide.}}{CuO} + H_2 = \underset{\text{Copper.}}{Cu} + H_2O.$$

Heat a weighed portion of cupric oxide (containing a definite amount of oxygen), in a stream of pure, dry hydrogen, and weigh the quantity of H_2O obtained. The operation can be executed in the apparatus represented in Fig. 57. The H generated in the flask *A* is washed in *B* and then dried in the tubes *C*, *D* and *E*, which contain substances that will absorb water. The bulb tube *F*, of difficultly fusible glass, contains a weighed amount of cupric oxide, and is heated with a lamp. The water which forms, collects in the bulb *G*, and is completely absorbed in the tube *H*. Hydrogen is led over the cupric oxide until it is reduced to red metallic copper, then allowed to cool, when *F* is weighed alone and *G* and *H* together. The loss in weight of *F* expresses the quantity of oxygen which has combined with hydrogen to produce water. The increase in weight of *G* and *H* gives the quantity of water that was formed. The difference shows the amount of H in water. Thus we ascertain that in 100 parts of water, by weight, there are:—

FIG. 57.



11.136	Parts	Hydrogen.
88.864	"	Oxygen.
100.000	"	Water.

Or, 1 part hydrogen and 7.98 parts oxygen yield 8.98 parts water.

THE MOLECULAR FORMULA OF WATER. ATOMIC WEIGHT OF OXYGEN.

If the molecule of water (like HCl) contains 1 atom H and 1 atom oxygen, then its chemical formula would be HO, and the atomic weight of oxygen would be = 8. Such a supposition has, however, not been proved by any facts. It would be just as likely that the formula HO_2 might be ascribed to the water molecule; then, the atomic weight of oxygen would be 4. According to the formula H_2O, the atomic weight of O would be 16, etc. (see p. 72). Analytical data give no decision. For the determination of the true molecular magnitude of water and atomic weight of oxygen, we must direct our attention to the views presented on pages 77-80. In equal volumes of all gases (or vapors) there is an equal number of molecules. The molecular weights, therefore, are proportional to the gas densities, and are equal to double that of the densities referred to H = 1.003. The density of steam is 9 (H = 1); the weight of the water molecule is therefore 18. Analysis, however, shows that in 18 parts water 2 parts by weight are hydrogen (= 2 atoms) and 16 parts oxygen by weight. According to this, the molecule of water contains not more nor less than 2 atoms of hydrogen. That the 16 parts of oxygen combined with the latter correspond to *one atom* (that the atomic weight does not equal the half, in which case the molecular formula of water would be H_2O_2), follows from the fact that the analysis of none of the innumerable oxygen derivatives has shown less than 16 parts oxygen in the molecule (see p. 80). *The molecular formula of water, therefore, is* $H_2O = 18$. The gas density of oxygen is 16, the molecular weight 32, therefore the *oxygen molecule consists of* 2 *atoms*, $O_2 = 32$.

After having thus derived the molecular formula of water, and the atomic weight of oxygen, we deduce the following conclusions:—

(1) 16 parts of O by weight, occupy the same volume as 1 part of H by weight; since 16 parts of the former unite with 2 parts of the latter in the production of water, 1 *volume* of O must combine with 2 *volumes* of H.

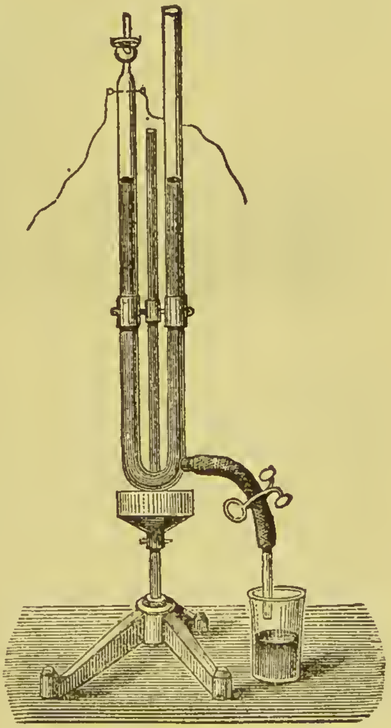
(2) In equal volumes we have an equal number of molecules; *n* molecules of oxygen (O_2) unite therefore with 2 *n* molecules of hydrogen (H_2); the same yield 2 *n* molecules of water; consequently 2 *volumes* of aqueous vapor:—

$$\underset{\text{2 vols.}}{2nH_2} + \underset{\text{1 vol.}}{nO_2} = \underset{\text{2 vols.}}{2nH_2O.}$$

According to the above, 2 *volumes of hydrogen and* 1 *volume of oxygen condense in their union to* 2 *volumes of aqueous vapor.*

The same result follows from the gas density of water. As 1 volume of steam weighs 9, and 2 parts of hydrogen by weight unite with 16 parts of oxygen by weight to form 18 parts of water; then, the latter, in the form of vapor, must occupy two volumes. Conversely from these volume ratios it is shown that the molecule of oxygen consists of two atoms (compare p. 78).

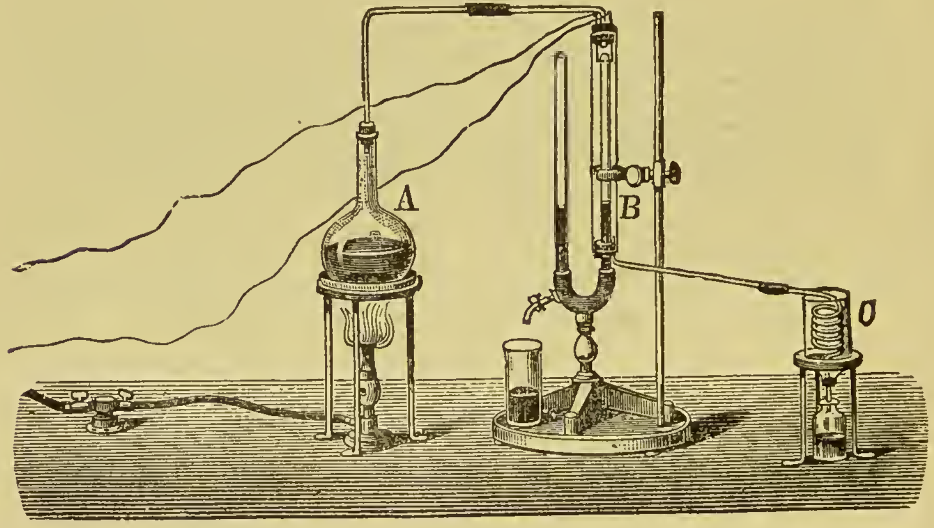
FIG. 58.



These conclusions are confirmed by the following experiments:—

1. When water is decomposed by the electric current in a voltameter, or, more suitably, in Hofmann's apparatus (Fig. 48, p. 76), it will be found that the volume of the separated hydrogen is double that of the oxygen. This can also be proved synthetically. Introduce 1 volume of oxygen and 2 volumes of hydrogen into a eudiometer tube filled with mercury (see Air), and let the electric spark pass through the mixture. This will unite the two gases, a small quantity of water forming at the same time; all the gas has disappeared, and the tube fills perfectly with mercury. In place of the eudiometer, the apparatus pictured in Fig. 58 may be advantageously employed in this experiment (and also in many others). It consists of a U-shaped glass tube, one limb of which, open above, is provided below with an exit tube. The other limb really represents a eudiometer; it is divided into cubic centimeters, having two platinum wires fused into the upper end, and provided with a stop-cock to let out the gases and thus test them. Fill the tube to the stop-cock with mercury, and run into the eudiometer limb 1 volume O and 2 volumes H. The side exit tube serves to run out the mercury to the same level in both tubes, so that the gases are always measured under the same atmospheric pressure, and thus their volumes are easily compared.

FIG. 59.



2. To determine the volume of the formed water existing as aqueous vapor it is only necessary, after the explosion, to convert it by heat into steam. The above apparatus will answer for this purpose (Fig. 59). This is essentially the same as that pictured in Fig. 58, with the eudiometer limb closed above and surrounded by a wider tube. Through the latter conduct the vapors of some liquid boiling above 100° C (aniline). These, then, pass through the envelope B, and are again condensed in the spiral tube C. The quantities of H and O used are heated to the same temperature, their volume noted, the explosion produced, and the volume of the resulting aqueous vapor determined. From this it is found that the volume of hydrogen is $\frac{2}{3}$ of the volume of the gas mixture; and 3 volumes of oxy-hydrogen gas yield 2 volumes of aqueous vapor.

The composition of water by weight may be easily deduced, knowing the specific gravities of hydrogen and oxygen and the ratios in which they unite by volume:—

1 volume of oxygen equals 16 parts by weight.
2 volumes of hydrogen equal 2.006 parts by weight.
The resulting H_2O equals 18.006 parts by weight.

18 parts water, therefore, contain 16 parts oxygen and 2 parts hydrogen, or, in 100 parts there are 88.18 parts oxygen and 11.12 parts hydrogen.

2. HYDROGEN PEROXIDE.

$H_2O_2 = 34$.

In addition to water, oxygen forms another compound with hydrogen, known as hydrogen peroxide. It is produced by the action of dilute acids upon certain peroxides, such as those of potassium, calcium and barium. It is most conveniently obtained by the action of hydrochloric acid upon barium peroxide :—

$$\underset{\text{Barium peroxide.}}{BaO_2} + 2HCl = \underset{\text{Barium chloride.}}{BaCl_2} + H_2O_2.$$

Barium peroxide made to a paste with a little water (better the hydrate—see Barium) is introduced gradually, in small quantities, into cold hydrochloric acid, diluted with three volumes of water. Hydrogen peroxide and barium chloride result; both are soluble in water. To remove the second from the solution, add to the latter a solution of silver sulphate as long as a precipitate is formed. Two insoluble compounds, barium sulphate and silver chloride, are produced by this reagent:—

$$BaCl_2 + Ag_2SO_4 = BaSO_4 + 2AgCl.$$

Remove the precipitate by filtration and concentrate the aqueous solution under the air pump. It now contains only hydrogen peroxide.

In making the peroxide, carbon dioxide may be allowed to act on barium peroxide suspended in water :—

$$BaO_2 + CO_2 + H_2O = BaCO_3 + H_2O_2.$$

The insoluble barium carbonate is filtered off and the filtrate concentrated.

Hydrogen peroxide is most practically obtained by adding moist barium hydrated peroxide (see Barium) to cold dilute sulphuric acid. The reaction occurs according to the following equation :—

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$

When the acid is almost neutralized, filter the solution, and from the filtrate carefully precipitate the slight quantity of free sulphuric acid with a dilute barium hydroxide solution, then concentrate the liquid under the air pump. Dry commercial hydrate of the peroxide of barium is not applicable for the above. A dilute solution of hydrogen peroxide is very readily prepared, if sodium peroxide (obtainable by fusing sodium in the air) is added to dilute tartaric acid.

Besides these decompositions of metallic peroxides, other methods exist for preparing hydrogen peroxide (in small quantity). Thus it arises frequently in slow oxidations, when ozone is also produced. If phosphorus, covered with water, be allowed to oxidize (p. 85) in the air, hydrogen peroxide will be found in the water, and the surrounding air will contain ozone. Or, if a flask filled with air be shaken with zinc and water or dilute sulphuric acid, hydrogen peroxide will be produced. It is destroyed again by the prolonged action of the zinc. Copper, lead, and other heavy metals do the same when agitated with more or less dilute sulphuric acid, and we find the same result by the oxidation of many organic substances, *e. g.*, pyrogallic acid and tannin on exposure to the air. In combustions, if the flame be cooled suddenly, we have formed, very often, slight quantities of hydrogen peroxide (and ozone), *e. g.*, in bringing a hydrogen or carbon monoxide flame in contact with water (Traube). The explanation offered for this formation of hydrogen peroxide (and ozone) is, that in the oxidations, the oxygen molecules are torn asunder, and the nascent oxygen atoms oxidize the water to a slight degree to hydrogen peroxide, and oxygen to ozone. The rare occurrence of ozone is due either to its difficult formation, or to the fact that it is readily decomposed by the reacting bodies (zinc, etc.). This is also the case with hydrogen peroxide. The appearance of hydrogen peroxide in the oxidation of phosphorus, seems to prove that it can be formed by the oxidation of water. This seems to be confirmed by its production on shaking turpentine oil with water and air, or if ozone be conducted into ether, and the ozonized product shaken with water (water is not directly oxidized by ozone.) It appears probable, however, that in some oxidation reactions, the formation of the hydrogen peroxide is a consequence of the *reduction* of oxygen (Traube). It may, for example, be assumed that when zinc (lead, iron) is shaken with air and water (or dilute sulphuric acid), the latter is decomposed in such a manner that the hydroxyl group combines with the zinc to hydroxide, and the liberated hydrogen then yields hydrogen peroxide with oxygen :—

$$Zn + 2OHH + O_2 = Zn(OH)_2 + H_2O_2.$$

A confirmation of this supposition is found in the electrolysis of water, where we discover H_2O_2 appearing at the negative pole (where hydrogen is found) if air or oxygen be conducted through the solution, $2H + O_2 = H_2O_2$. It is verified, too, in the production of H_2O_2 upon shaking palladium hydride with water and air :—

$$2Pd_2H + O_2 = 4Pd + H_2O_2.$$

The excess of palladium hydride further decomposes the peroxide that was formed :—

$$2Pd_2H + H_2O_2 = 4Pd + 2H_2O.$$

In all these examples we can explain the formation of the peroxide by the action of nascent hydrogen upon oxygen. It is, however, not true that hydrogen peroxide is formed only by the reduction of molecular oxygen (see above). An evidence of this is the fact that hydrogen peroxide is produced at the anode in the electrolysis of sulphuric acid; its appearance here is due to the decomposition of the persulphuric acid (S_2O_7 or $S_2O_8H_2$—see this (Richarz).

The production of hydrogen peroxide in oxidations and combustions as an intermediate product has led to the assumption that all oxidations are conditioned by the transitory formation of hydrogen peroxide—Traube's oxidation theory. It was supposed that the proof of this could be found in the circumstance that various oxidations, *e. g.*, the union of carbon monoxide with oxygen to form CO_2—could only occur with ease in the presence of aqueous vapor (Dixon) : $CO + 2OHH + O_2 = CO_2 + H_2O + H_2O_2$. More careful investigations have, however, demonstrated that the presence of moisture is not necessarily essential in oxidations. Carbon monoxide and oxygen also combine to carbon dioxide when perfectly dry if the temperature be sufficiently high. Their union in the presence of moisture is due solely to the fact that the following transpositions, $CO + H_2O = CO_2 + H_2$ and $2H_2 + O_2 = 2H_2O$, take place more readily and at a lower temperature than the direct union of carbon monoxide with oxygen : $2CO + O_2 = 2CO_2$ (Lothar Meyer).

Hydrogen peroxide, concentrated as much as possible under the air pump, is a colorless, syrupy liquid, with a specific gravity of 1.45, and does not solidify at—30° C.; from very dilute solutions, pure water freezes out. It possesses a bitter, astringent taste, is miscible in all proportions with water, and vaporizes in vacuo. Very dilute aqueous solutions can be boiled without decomposing the peroxide; a portion of it distils over with the water.

In concentrated solutions, hydrogen peroxide is very unstable, and easily decomposed with liberation of oxygen; in more dilute acidulated solutions it may be preserved longer. Decomposition occurs, even at ordinary temperatures; by heating the point of explosion can be reached. In consequence of this ready decomposition, hydrogen peroxide oxidizes powerfully, since oxygen appears (p. 79) in *statu nascendi*. It converts selenium, chromium, and arsenic into their corresponding acids; sulphides are changed to sulphates (PbS to $PbSO_4$); from lead acetate solutions the peroxide is precipitated, but is again decolorized by the excess of peroxide. Organic dyestuffs are decolorized and decomposed. From hydrogen sulphide, sulphur, from hydrogen chloride and iodide, chlorine and iodine are set free :—

$$H_2O_2 + 2HI = 2H_2O + I_2.$$

Thus hydrogen peroxide acts in a manner analogous to ozone; in both there exists a slightly bound atom of oxygen, which can readily be transferred to other bodies.

Hydrogen peroxide acts very slowly upon a neutral potassium iodide solution, while ozone separates iodine at once; but if platinum-black, ferrous sulphate, or blood corpuscles (see p. 88), be added to the solution, iodine immediately separates out, and colors added starch paste a deep blue.

In all these cases the action of hydrogen peroxide is oxidizing. Some substances, on the other hand, are reduced by it, oxygen separating at the same time; this is true of certain unstable oxides, peroxides, and the highest oxidations of some metals, like Mn_2O_7, and CrO_3. Thus, argentic, mercuric, and gold oxides are reduced to a metallic state with an energetic evolution of oxygen :—

$$Ag_2O + H_2O_2 = 2Ag + H_2O + O_2.$$

Lead peroxide is changed to lead oxide :—

$$PbO_2 + H_2O_2 = PbO + H_2O + O_2.$$

In the presence of acids, the solution of potassium permanganate is decolorized and changed to a manganous salt (p. 104). In the same way chromic acid and its salts are altered to chromic oxide :—

$$2CrO_3 + 3H_2O_2 = Cr_2O_3 + 3H_2O + 3O_2.$$

Ozone and hydrogen peroxide decompose themselves into water and oxygen:—

$$O_3 + H_2O_2 = O_2 + H_2O + O_2.$$

Chlorine in aqueous solution is oxidized to hypochlorous acid by hydrogen peroxide, $Cl_2 + H_2O_2 = 2HOCl$, but again reduced by an excess of the latter:—

$$ClOH + H_2O_2 = ClH + H_2O + O_2.$$

All these reactions are generally explained by supposing that the oxygen atoms (also those of other elements), possess a certain affinity for each other; this is saturated by their union to molecules. Those present in other compounds, and not firmly bound, therefore separate and unite with each other, and form free oxygen molecules—OO. The conclusion derived from the gas density, viz., that the molecules of the free elements consist of two or more atoms, is corroborated by these reactions. The readiness with which ozone and hydrogen peroxide react, is explained by their thermo-chemical behavior.

Hydrogen peroxide, like ozone (p. 88), is an endothermic compound when compared with water, *i. e.*, it contains more energy than the latter:—

$$(H_2O, O) = -23.07 \text{ Cal.}$$

It can only be produced from water by the addition of energy from without, and it reverts again to it with the liberation of heat. Oxidations with hydrogen peroxide, as with ozone, proceed more readily and more energetically than with oxygen.

Finally, hydrogen peroxide may be decomposed into water and oxygen by many bodies, especially when the latter exist in a divided condition, and they themselves are not in the least altered. Gold, platinum, silver, manganese peroxide, carbon and others, act in this way. Such reactions, in which the reacting substances undergo no perceptible changes, are designated *catalytic*. In many cases these may be explained by the previous formation of intermediate products, which subsequently react upon each other. Thus, we can suppose that in the action of silver and gold upon H_2O_2 oxides at first result, but are afterward reduced in the manner mentioned above, by the hydrogen peroxide.

REACTIONS FOR THE DETECTION OF HYDROGEN PEROXIDE.

H_2O_2 decomposes potassium iodide very slowly; in the presence of iron sulphate, however, iodine separates at once, and is recognized by the blue color it yields with starch paste. In the same way guaiacum tincture, in the presence of ferrous sulphate, is immediately colored blue, and an indigo solution is decolorized. The most characteristic test for the peroxide is the following: Introduce some H_2O_2 into a chromic acid solution, add a little ether and shake thoroughly; the supernatant ethereal layer will be colored blue (compare Chromic acid.)

A solution of titanic acid in sulphuric acid (diluted strongly with water), is also a delicate reagent; traces of it afford an orange yellow color with hydrogen peroxide.

Hydrogen peroxide is determined quantitatively by oxidation with potassium permanganate (see Manganese). The latter is added to the solution, acidified with sulphuric acid, until a permanent coloration occurs. The reaction proceeds according to the equation:—

$$2MnO_4K + 3SO_4H_2 + 5H_2O_2 = 2SO_4Mn + SO_4K_2 + 8H_2O + 5O_2.$$

Or the liquid to be examined (rain water) for hydrogen peroxide is shaken in a stoppered glass with a five per cent. solution of potassium iodide and some starch paste, allowed to stand several hours, and the iodine which separates is then determined colorimetrically (Schöne).

Thermo-chemical Deportment.—The great reactivity of hydrogen peroxide, its various modes of formation and its transpositions are fully explained by its thermal relations. Compared with water, it, like ozone, is an endothermic compound, *i.e.*, it contains more energy than water: $(H_2O,O) = -23.07$ Cal. Therefore, its formation from the latter requires the addition of energy. Its production by the oxidation of water is exceptional, and occurs with difficulty. It loses energy (heat) and readily changes to more stable water. Like ozone, its oxidations proceed more energetically than those with free oxygen, because 23.07 Cals. more are disengaged.

The production of hydrogen peroxide by the transposition of barium peroxide and hydrochloric acid (p. 101) accords with the principle of greatest heat liberation, as heat is set free in this reaction (22.0 Cal.) according to the equation: $BaO_2 + 2HCl, Aq = BaCl_2, Aq + H_2O_2$ . . . . + 22.0 Cal.

Hydrogen peroxide is similarly formed from other peroxides, *e.g.*, potassium, calcium, and zinc peroxides, which are decomposed by acids with the disengagement of heat, yet the superoxides or dioxides of manganese and lead (MnO_2 and PbO_2) do not yield hydrogen peroxide. This is due to the fact that heat must be absorbed (Berthelot).

Hydrogen peroxide occurs in slight quantity in the air and is detected in almost all rain water and in snow—but not in natural dew and frost. Its quantity varies from 0.05 to 1 milligram in a litre of rain. Its formation in the air is probably induced by the action of ozone upon ammonia, whereby ammonium nitrite, hydrogen peroxide and oxygen result (Carius).

Analysis shows that H_2O_2 consists of 1 part hydrogen and 16 parts of oxygen; its simplest formula would therefore be HO. The difficult volatility of the compound, and also the reactions already described, cause us to believe that the molecule of hydrogen peroxide is more complicated, and is expressed by H_2O_2. It is supposed that the peroxide is composed of two groups of OH, called *hydroxyl;* these are combined with each other.

3. SULPHUR.

$S = 32.06$. $S_2 = 64.12$ (above 1000° C.).

Sulphur is distributed throughout nature, both free and in a combined state. In volcanic regions, like Sicily, it occurs free, and there it forms vast deposits, mixed with gypsum, calcite and marl. Its compounds with the metals are known as blendes or glances. In combination with oxygen and calcium, it forms calcium sulphate, the widely distributed gypsum. It is also present in many organic substances.

To obtain sulphur, the natural product in Sicily is arranged in heaps, covered with earth and then melted, or it is distilled from earthen retorts. To further purify this crude commercial product it is redistilled (in the manufactory) from cast-iron retorts, and when in a molten condition is run into cylindrical forms—*stick sulphur.* If the sulphur vapors are rapidly cooled during distillation (which occurs by conducting them into a stone chamber through which cold air circulates), they condense to a fine yellow powder, known as *flowers of sulphur* (Flores sulphuris).

Sulphur may be obtained by heating the well-known pyrites (FeS_2).

Free sulphur exists in several allotropic modifications (see p. 88).

1. *Ordinary octahedral* or *rhombic sulphur* exists in nature in beautiful, well-crystallized rhombic octahedra (Figs. 21 and 22, p. 36). It is pale yellow, hard and very brittle; on rubbing, it becomes negatively electrified. Specific gravity of this variety equals 2.05. It dissolves with difficulty in alcohol and ether; but is more readily soluble in hydrocarbons and ethereal oils. The best solvents are sulphur monochloride (S_2Cl_2) and carbon disulphide (CS_2); 100 parts of the latter at 22° C., dissolve 46 parts of sulphur. By slow evaporation of the solutions sulphur crystallizes in transparent, lustrous, rhombic octahedra, like those occurring in nature. Sulphur fuses at 111.5° C. (113° C.), to a yellow, mobile liquid, which upon further heating becomes dark and thick, and at 250° C., is so viscid that it cannot be poured from the vessel holding it. Above 300° C., it again becomes a thin liquid, boils at 440° C., and is converted into an orange-yellow vapor.

2. The *prismatic* or *monoclinic sulphur* is obtained from the rhombic when the latter is heated to its point of fusion; on cooling it generally assumes the monoclinic form (rhombic crystals separate at 90° from sulphur that has been heated beyond the point of fusion). The monoclinic crystals are best obtained as follows: Fuse sulphur in a clay crucible, allow it to cool slowly until a crust appears on the surface; break this open near the side and pour out the portion yet in a liquid state. The walls of the crucible will be covered with long, somewhat curved, transparent, brownish-yellow needles, or prisms of the monoclinic system. The same are obtained when a solution of sulphur in carbon disulphide is heated to 100° C., in a sealed tube, and then gradually allowed to cool; monoclinic crystals at first separate, and later, at low temperatures, rhombic octahedra. The monoclinic crystals separated from the solution are almost colorless and perfectly transparent.

Prismatic or octahedral crystals may be obtained from a supersaturated benzene solution of sulphur, by adding small fragments of the corresponding crystals to the solution.

This form of sulphur has a specific gravity of 1.96 and fuses at 120°. It is soluble in the same solvents as the rhombic variety. It is very unstable; the transparent prisms and needles become opaque and pale yellow at ordinary temperatures, and specifically heavier (heat is evolved), and pass over into an aggregate of rhombic octahedra retaining the external prismatic form. Stick sulphur deports itself similarly; the freshly moulded sticks are composed of monoclinic prisms, but in time their specific gravity changes and they are converted into the rhombic modification.

3. *Soft, plastic sulphur* appears to consist of two modifications. It is obtained when sulphur heated above 230° is poured in a thin stream into water; it then forms a soft, fusible mass, of a yellowish-brown color, and its specific gravity equals 1.96. In a few days it hardens, and is converted into the rhombic variety. At 95° the conversion is instantaneous and accompanied by the evolution of considerable heat. It is only partly soluble in carbon disulphide, leaving an amorphous powder undissolved—amorphous insoluble sulphur. It is also produced when light acts upon dissolved or fused sulphur, and in the decomposition of the halogen-sulphur compounds by H_2O. Flowers of sulphur are for the most part insoluble in carbon disulphide. 100° C. will convert the amorphous insoluble sulphur into the ordinary variety.

On adding hydrochloric acid to polysulphide solutions of potassium or calcium, sulphur separates as a fine, white powder, known as *milk of sulphur* (Lac sulphuris):—

$$K_2S_5 + 2HCl = 2KCl + H_2S + 4S.$$

This is amorphous, soluble in carbon disulphide, and gradually passes into the rhombic form.

The existence of these various modifications of sulphur, like ozone, may be attributed to the presence of a varying number of atoms in the molecules. This supposition is confirmed by the deportment of sulphur vapor. The density of the latter at 500° C., has been found to equal 96 ($H = 1$). The vapor density steadily diminishes with increase of temperature from 700° C. onward and becomes constant at 1000° C., and equals 32; the molecular weight, therefore, is 64. Since the atomic weight of S (as we will see) $= 32$, it follows that at 1000° C., the molecules of S consist of two atoms ($S_2 = 64 = 32 \times 2$). At 500°, however, where the vapor density $= 96$, and the molecular weight 192, the molecule consists of six atoms ($S_6 = 6 \times 32 = 192$). According to this the hexatomic sulphur molecules dissociate (see p. 94), on further heating, and fall into normal diatomic molecules; the dissociation begins at 700° and is complete at 1000° C. Since, therefore, the sulphur molecules in vapor form consist of two atoms at very high temperatures and of six atoms at lower, we may assume that the molecules in the liquid and solid condition are more complicated, and that the various allotropic modifications are influenced by the number of atoms contained in the molecules. Other solid metalloids, *e. g.*, selenium, phosphorus, arsenic, carbon and silicon, occur in different modifications. As yet we have no means of ascertaining the molecular size of the elements in liquid and solid conditions; there is much, however, favoring the idea that when free they consist of complex atomic groups.

Chemical Properties.—In its chemical behavior sulphur is very similar to oxygen. It unites directly with most of the elements. When heated to 260° in the air, it ignites and burns with a pale bluish flame, forming sulphur dioxide (SO_2). This union with oxygen occurs gradually even at lower temperatures (about 180°); in the dark it is accompanied by a white phosphorescent flame. Nearly all the metals combine with it to form sulphides. By rubbing mercury, flowers of sulphur and water together, we obtain black mercury sulphide. A moist mixture of iron filings and sulphur glows after a time. Cu and Fe burn in sulphur vapor. The sulphides are analogous to the oxides, exhibit similar reactions, and in the main possess a similar composition, as may be seen from the following formulas:—

H_2O,	Water.	H_2S,	Hydrogen sulphide.
KOH,	Potassium hydrate.	KSH,	Potassium sulphydrate.
BaO,	Barium oxide.	BaS,	Barium sulphide.
CO_2,	Carbon dioxide.	CS_2,	Carbon disulphide.
CO_3K_2,	Potassium carbonate.	CS_3K_2,	Potassium sulpho-carbonate.

COMPOUNDS OF SULPHUR WITH HYDROGEN.

1. HYDROGEN SULPHIDE.

$H_2S = 34.06$. Density $= 17.03$.

In nature hydrogen sulphide occurs principally in volcanic gases and in the so-called sulphur waters. It is always produced in the decomposition of organic substances containing sulphur, and in the reduction of alkaline sulphates by decomposing carbon compounds. It may be formed directly from its constituents, although in small quantity, if hydrogen gas be conducted through boiling sulphur, or if sulphur vapors, together with hydrogen, be conducted over porous substances (pumice stone, bricks) heated to 500° C. Many sulphides are reduced upon ignition in a stream of hydrogen, with separation of hydrogen sulphide:—

$$Ag_2S + H_2 = 2Ag + H_2S.$$

For its production acids are allowed to act upon sulphides. Ordinarily iron sulphide and diluted sulphuric acid are employed: the action occurs at ordinary temperatures:—

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

The operation is performed either in Kipp's apparatus (p. 42) or in the one pictured in Fig. 30.

Hydrogen sulphide thus obtained contains admixed hydrogen, in consequence of metallic iron existing in the sulphide. The pure gas is obtained by heating antimony sulphide with hydrochloric acid:—

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

Properties.—Hydrogen sulphide is a colorless gas, having an odor similar to that of rotten eggs; inhaled in large quantities it has a stupefying effect, and is very poisonous. At medium temperatures it condenses under a pressure of 14 atmospheres (under ordinary pressure at —74°) to a colorless liquid of specific gravity 0.9, which at — 85° C. solidifies to a white crystalline mass. Its density equals 16.99 ($H = 1$) or 1.177 (air = 1). Water dissolves 3–4 times its volume of gas; the solution possesses all the properties of gaseous hydrogen sulphide and is therefore called hydrogen sulphide water.

Ignited in the air the gas burns with a blue flame, water and sulphur dioxide resulting:—

$$H_2S + 3O = H_2O + SO_2.$$

With sufficient air access, or when the flame is cooled by the introduction of a cold body, only hydrogen burns and sulphur separates out in a free condition. In aqueous solution hydrogen sulphide is decomposed by the oxygen of the air at ordinary temperatures, sulphur separating as a fine powder:—

$$H_2S + O = H_2O + S.$$

For this reason hydrogen sulphide becomes turbid upon exposure to the air.

The halogens behave like oxygen; the hydrides of the halogens are formed with separation of sulphur:—

$$H_2S + I_2 = 2HI + S.$$

This reaction serves for the production of hydrogen iodide (p. 63).

As hydrogen sulphide has a great affinity for oxygen, it withdraws the latter from many of its compounds, and it therefore acts as a reducing agent (p. 85). Thus chromic, manganic and nitric acids are reduced to lower stages of oxidation. On pouring fuming nitric acid into a vessel filled with the dry gas, the mixture will ignite with a slight explosion.

Hydrogen sulphide possesses weak acid properties, reddens blue litmus paper, forms salt-like compounds with bases, and is, therefore, termed hydrosulphuric acid. Nearly all the metals liberate hydrogen from it, yielding metallic sulphides:—

$$Pb + H_2S = PbS + H_2.$$

With the oxides and hydroxides of the metals H_2S yields sulphides and sulphydrates:—

$$\mathrm{KOH} + \mathrm{H_2S} = \underset{\substack{\text{Potassium}\\ \text{hydrosulphide.}}}{\mathrm{KSH}} + \mathrm{H_2O}.$$

$$\mathrm{CaO} + \mathrm{H_2S} = \underset{\substack{\text{Calcium}\\ \text{sulphide.}}}{\mathrm{CaS}} + \mathrm{H_2O}.$$

Sulphides, therefore, like the compounds of the halogens with the metals, may be viewed as the salts of hydrosulphuric acid. The sulphides of almost all the heavy metals are insoluble in water and dilute acids; therefore they are precipitated by H_2S from solutions of metallic salts:—

$$\mathrm{CuSO_4} + \mathrm{H_2S} = \mathrm{CuS} + \mathrm{H_2SO_4}.$$

The precipitates thus obtained are variously colored (copper sulphide, black; cadmium sulphide, yellow; antimony sulphide, orange), and answer for the characterization and recognition of the corresponding metals. Paper saturated with a lead solution is at once blackened by H_2S, lead sulphide being formed—a delicate test for H_2S.

Thermo-chemical Deportment.—Hydrogen sulphide is a feebly exothermic compound. When hydrogen gas unites with solid sulphur to form hydrogen sulphide 4.5 Cal. are developed. When the gas dissolves in much water its heat of solution rises to + 4.7 Cal., so that the heat of formation of hydrogen sulphide in dilute aqueous solution equals in all 9.2 Cal.:—

$$(\mathrm{H_2,S} \text{ — gas}) = 4.5; \quad (\mathrm{H_2S, Aq.}) = 4.7; \quad (\mathrm{H_2, S, Aq.}) = 9.2.$$

It is because of this low heat of formation that the gas is produced with such difficulty from its elements, and it is for this reason that it is so readily dissociated by heat into its elements. Its entire chemical deportment is also accounted for by its heat of formation (p. 115).

MOLECULAR FORMULA OF HYDROGEN SULPHIDE. ATOMIC WEIGHT OF SULPHUR.

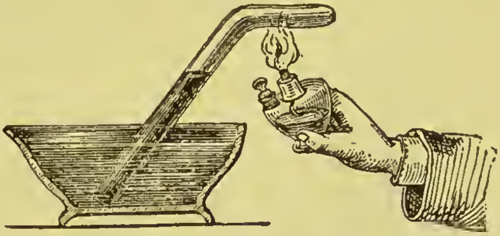
The analysis of hydrogen sulphide shows that it consists of one part hydrogen and sixteen (more accurately 16.03) parts sulphur. If the molecular formula of hydrogen sulphide were HS, the atomic weight of sulphur would be sixteen (compare p. 98). The great analogy of the sulphur compounds with those of oxygen (p. 108), permits us to accept formulas for the former similar to those of the latter. The molecular formula of hydrogen sulphide would, therefore, be $H_2S = 34.06$, and the atomic weight of sulphur would equal 32.06. Hence the gas density of hydrogen sulphide must be $\frac{34}{2} = 17$ ($H = 1$), or 1.177 (air = 1); this is confirmed by direct experiment. Conversely, it follows from the gas density that the molecular weight of hydrogen sulphide = 34.06. Since the analysis of 34.06 parts of hydrogen sulphide shows the presence of two parts of hydrogen, the molecule of H_2S contains two hydrogen atoms. It then follows that the 32.06 parts of sulphur combined with the latter, correspond to *one* atom of sulphur, because less than 32.06 parts of this element have never been found in the molecule of any compound in which sulphur occurs (p. 80).

From the molecular formula H_2S, we further conclude that the hydrogen contained in one volume of hydrogen sulphide would occupy in a free condition the same volume as the latter: —

$$\underset{\text{1 vol.}}{nH_2S} \text{ contains } \underset{\text{1 vol.}}{nH_2}.$$

This conclusion is verified experimentally as follows: In a bent glass tube filled with mercury (Fig. 60), introduce dry hydrogen sulphide gas; then in the bent portion place a piece of tin, which is heated by a lamp. The sulphur of the H_2S combines with the metal to form solid tin sulphide, while hydrogen is set free: its volume is exactly equal to the volume of the employed hydrogen sulphide. The quantity of sulphur, 32 parts, in vapor form, at 1000° C., when the density is 32 (p. 107) combined with hydrogen (2 parts) would equal exactly half the volume of the hydrogen; at 500° C., however, when the vapor density is three times as great, it will equal 1/6 volume of the hydrogen. 1 volume H_2S, therefore, consists of 1 volume H and 1/6 volume sulphur vapor (at 500°), or as ordinarily expressed: 2 volumes H_2S consist of 2 volumes H and 1/3 volume sulphur vapor. Written molecularly, we have :—

FIG. 60.



$$\text{At 500° C.: } \underset{\text{1 vol.}}{S_6} + \underset{\text{6 vols.}}{6H_2} = \underset{\text{6 vols.}}{6H_2S}.$$

$$\text{At 1000° C., however: } \underset{\text{1 vol.}}{S_2} + \underset{\text{2 vols.}}{2H_2} = \underset{\text{2 vols.}}{2H_2S}.$$

2. HYDROGEN PERSULPHIDE.

Just as hydrogen peroxide H_2O_2 is formed by (p. 101) the action of acids upon some peroxide, so may hydrogen persulphide be obtained from metallic persulphides. Calcium persulphide is most suitable, and when its aqueous solution is poured into dilute hydrochloric acid,

$$CaS_2 + 2HCl = CaCl_2 + H_2S_2,$$

a yellow, oily, disagreeable liquid, insoluble in water, separates. It decomposes gradually at medium temperatures, more rapidly on warming, into hydrogen sulphide and sulphur :—

$$H_2S_2 = H_2S + S.$$

It is generally supposed that the resulting hydrogen persulphide is similar in constitution to the peroxide and consists of *hydrogen disulphide*, containing an excess of dissolved sulphur.

As the calcium persulphide used is a mixture of CaS_2, CaS_3, and CaS_5, it is probable that the oily liquid is a mixture of H_2S_2, H_2S_3 and H_2S_5. We must at least conclude that H_2S_3 is present in it, because it unites with strychnine to form a crystalline compound.

COMPOUNDS OF SULPHUR WITH THE HALOGENS.

Sulphur and chlorine unite to form three compounds: SCl_2, SCl_4, and S_2Cl_2.

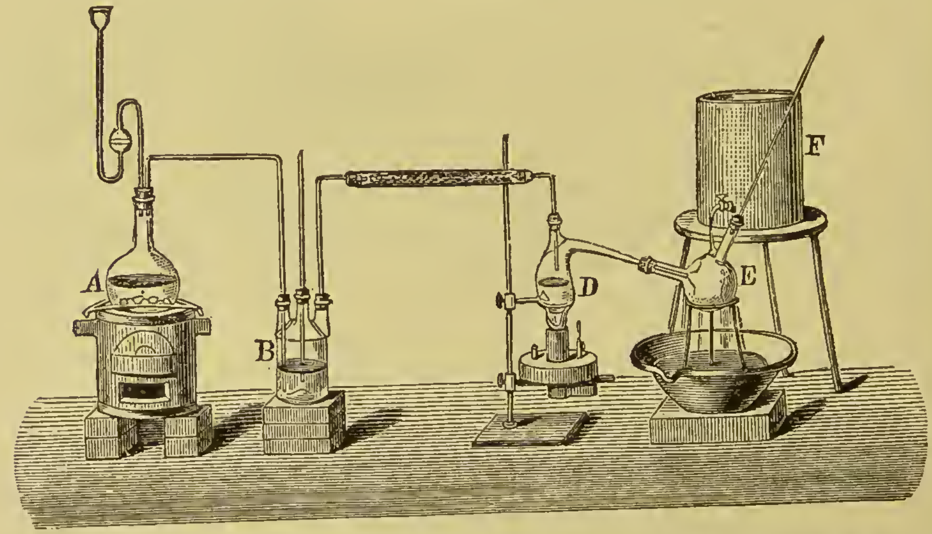
It is only the latter that meets with any practical application.

Sulphur Dichloride—SCl_2—is produced when S_2Cl_2 is saturated with chlorine in the cold:—

$$S_2Cl_2 + Cl_2 = 2SCl_2.$$

The excess of chlorine is removed by conducting a stream of CO_2 through it.

Fig. 61.



It is a dark red-colored liquid, with a specific gravity of 1.62; boils at 64° C., with partial decomposition into S_2Cl_2 and Cl_2; the dissociation commences at ordinary temperatures.

Sulphur Tetrachloride—SCl_4—only exists at temperatures below 0° C. It is formed by saturating SCl_2 with Cl at −30° C., and readily decomposes into SCl_2 and Cl_2; the dissociation commences at −20° C., and is complete at + 6°. It yields crystalline compounds with some chlorides, *e. g.*, $SnCl_4$, $AsCl_3$, $SbCl_3$.

The most stable of the sulphur chlorides is

Sulphur Mono-chloride—S_2Cl_2—which is formed when chlorine is conducted over molten sulphur. (Fig. 61.) It distils over and condenses in the receiver *E*; the product is redistilled, to obtain it pure.

Sulphur mono-chloride is a reddish-yellow liquid with a sharp odor, provoking tears, having a specific gravity of 1.68, and boiling at 139° C. Its vapor density equals 67 ($H = 1$), corresponding to the molecular formula $S_2Cl_2 = 134.7$. It fumes strongly in the air, and is decomposed by water into sulphur dioxide, sulphur and hydrochloric acid:—

$$2S_2Cl_2 + 2H_2O = SO_2 + 4HCl + 3S.$$

Sulphur mono-chloride dissolves sulphur readily and serves in the vulcanization of caoutchouc.

Bromine forms analogous compounds with S. S_2Br_2 is a red liquid, boiling at 190°–200° C. When gently heated, iodine unites with S to form S_2I_2.

---

3. SELENIUM.

$Se = 79.1$. $Se_2 = 158.2$. (at 1400° C.).

This element is not very abundant in nature, and is only found in small quantities, principally in certain iron pyrites (in Sweden and Bohemia). Upon roasting this ore of iron, for the preparation of sulphuric acid, selenium settles out in the chimney dust or in the deposit of the lead chambers (compare Sulphuric Acid), and was found there by Berzelius, in the year 1817.

Like sulphur, selenium forms different allotropic modifications. *Amorphous selenium*, obtained by the reduction of selenium dioxide (SeO_2) by means of sulphur dioxide (SO_2), is a reddish-brown powder, soluble in carbon disulphide, and has a specific gravity of 4.26. Selenium crystallizes from carbon disulphide in brownish-red crystals, The solution of potassium selenide is brown-red, and when it is exposed to the air, black leaf-like crystals of selenium separate. These are isomorphous with sulphur. Upon suddenly cooling fused selenium it solidifies to an amorphous, glassy, black mass, which is soluble in carbon disulphide and has a specific gravity of 4.28. When selenium (amorphous) is heated to 97° C., its temperature suddenly rises above 200° C.; it is converted into a crystalline, dark gray mass with a specific gravity of 4.8. It possesses metallic lustre, conducts electricity, and is insoluble in carbon disulphide. The crystalline, insoluble modification is obtained by slowly cooling the molten selenium.

Selenium melts at 217°, and boils at about 700°, passing into a dark yellow vapor. The vapor density diminishes regularly with increasing temperature (similar to sulphur), and becomes constant at 1400° C. It then equals 79; the molecular weight is, therefore, 158, *i. e.*, the molecule of selenium at 1400° C., consists of two atoms ($2 \times 79.1 = 158.2$).

Selenium is a perfect analogue of sulphur. In the air it burns with a reddish-blue flame, forming SeO_2, and emits a peculiar odor resembling rotten horse-radish. It dissolves with a green color in concentrated sulphuric acid, and forms selenious acid.

Hydrogen Selenide—H_2Se—produced, like hydrogen sulphide, from iron selenide and hydrochloric acid—is a colorless, disagreeably smelling gas with poisonous action. In the air the aqueous solution becomes turbid and free selenium separates.

With chlorine selenium forms $SeCl_4$ and Se_2Cl_2, perfectly analogous to the sulphur compounds. $SeCl_4$ is a solid and sublimes without decomposition.

4. TELLURIUM.

Te = 125.*

Tellurium is of rare occurrence, either native or in combination with metals. It is associated with gold and silver in sylvanite, and with silver and lead in altaite. It is found principally in Transylvania, Hungary, California, Virginia, Bolivia and Brazil.

The tellurium precipitated by sulphurous acid from a solution of tellurous acid (see this) is a black powder of specific gravity 5.928.

The physical properties of tellurium indicate it to be a metal. It is silver white, of a perfect metallic lustre, and conducts electricity and heat. It crystallizes in rhombohedra, having a specific gravity 6.25. It fuses at 500° and vaporizes in a stream of hydrogen. When heated in the air it burns, with a bluish-gray flame, to tellurium dioxide (TeO_2).

The vapor density of tellurium at 1380° C., has been discovered to be about 126, corresponding to the molecular formula Te_2.

Hydrogen Telluride, H_2Te, formed by the action of hydrochloric acid upon zinc telluride, is a colorless, very poisonous gas, with disagreeable odor. Two chlorides—$TeCl_2$ and $TeCl_4$—and two bromides—$TeBr_2$ and $TeBr_4$—have been formed.

SUMMARY OF THE ELEMENTS OF THE OXYGEN GROUP.

The elements oxygen, sulphur, selenium and tellurium form a natural group of chemically similar bodies. The similarity of the last three is especially marked, while oxygen, possessing the lowest atomic weight, stands somewhat apart. Among the halogens, fluo-

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* The atomic weight of tellurium was first made 128 and subsequently 126.8. But the later development of the periodic system made it more probable that it was even lower than the atomic weight of iodine (126.5), which view has since been confirmed experimentally.

rine exhibits a similar deportment; it departs somewhat from its analogues, chlorine, bromine and iodine. Like the latter, the elements of the oxygen group present a gradation in their properties corresponding to their atomic weights:—

	O.	S.	Se.	Te.
Atomic weights,	16	32.06	79.1	125.

With the increase in the atomic weight there occurs a simultaneous condensation of substance, the volatility diminishes, while the specific gravity and the points of fusion and boiling increase, as may be seen in the following table:—

	Oxygen.	Sulphur.	Selenium.	Tellurium.
Specific gravity......	...	1.95–2.07	4.2–4.8	6.2
Melting point.........	...	111.5°	217°	500°
Boiling point..........	...	440°	700°	White heat.
Gas density...........	16	32	79	125

Oxygen is a difficultly coercible gas, while the others are solids at ordinary temperatures, We must, however, bear in mind that sulphur, selenium and tellurium in a free state are probably composed of larger complex atomic groups (see p. 107).

Further, with rising atomic weight the metalloidal passes into a more metallic character. Tellurium exhibits the physical properties of a metal; even selenium possesses metallic properties in its crystalline modification. In chemical deportment, however, the metalloidal character shows scarcely any alteration. All four elements unite directly, at elevated temperatures, with two atoms of hydrogen, to form volatile gaseous compounds having an acid nature; only the oxygen derivative—water—is liquid at ordinary temperatures and shows a neutral reaction. The hydrogen compounds are decomposed into their elements at a red heat. The affinity of hydrogen for oxygen is greatest; therefore, the aqueous solutions of H_2S, H_2Se and H_2Te are decomposed by the oxygen of the air.

Thermo-chemical Deportment.—A better explanation of the chemical behavior of these compounds is afforded by their thermo-chemical relations. The heat of formation of the hydrides of the elements of the oxygen group corresponds to the symbols (pp. 94 and 110):—

$$(H_2,O\text{-vapor}) = 57.2;\ (H_2,S) = 4.5;\ (H_2,Se) = -5.4.$$

We again observe a gradation similar to that noticed with the halogen hydrides (p. 66); in general it corresponds to the increasing metallic character of the elements. While water is a strongly exothermic compound, the hydrides of selenium and tellurium are produced with heat absorption, and are consequently not very stable. In accord with this we find that either oxygen or air will displace these elements from H_2S, H_2Se, and H_2Te when in aqueous solution with the formation of water. At higher temperatures and with an excess of oxygen the higher oxides (SO_2, SeO_2) also result. The halogens decompose them more readily than oxygen, forming the halogen hydrides at the same time (p. 68). The behavior of hydrogen sulphide in reference to the metals and their derivatives is especially well accounted for by its thermo-chemical relations (compare behavior of water toward metals, p. 94). This will receive further notice in the groups of metals.

As in the case of the halogen hydrides (p. 66), we may regard the heat of formation of compounds as a measure of the chemical energy of the elements composing them, but it is only a relative measure. Hydrogen and oxygen unite to form water according to the following molecular equation:—

$$2H_2 + O_2 = 2H_2O.$$

Evidently the molecules of hydrogen and oxygen must be split into their atoms, and this will require a definite quantity of heat, so that the true heat of union of 2H with O must exceed the observed by 57.2 calories. The observed only indicates that the affinity of hydrogen for oxygen (2H,O) is greater than the affinity of the hydrogen and oxygen atoms in their molecules:—

$$2(H_2,O) = 2(H,H) + (O,O) + 2 \times 57.2 \text{ Cal.}$$

In the production of hydrogen sulphide from its elements the first essential is the gasifying of the sulphur, and in doing this the latent heat of evaporation of sulphur is consumed. And then the hexatomic molecules (p. 107) must be separated into their individual atoms, which will require a quantity of heat exceeding the heat of decomposition of the diatomic oxygen molecules. This would show that the heat of formation of 2H with S must far exceed the observed heat of formation of hydrogen sulphide, which is only 4.5 Cal. The heat of absorption observed in the production of hydrogen selenide may be analogously explained by the greater heat of evaporation and decomposition of the selenium molecules.

That heat is absorbed in the breaking of the molecules, follows, among others, from the fact that, in the process of combustion in nitric oxide (NO), more heat will be set free than in oxygen (O_2). The energy-content of NO is greater than that of O_2. All the affinity masses derived from thermal data are, therefore, only relative; it is only recently that it has become possible to determine the heat of dissociation of the hydrogen molecules (H,H) = 128,000, and that of carbon (see Carbon Monoxide).

NITROGEN GROUP.

This group consists of nitrogen, phosphorus, arsenic, antimony, and bismuth. The latter possesses a decidedly metallic character. These elements, bismuth excepted, form gaseous derivatives with three atoms of hydrogen.

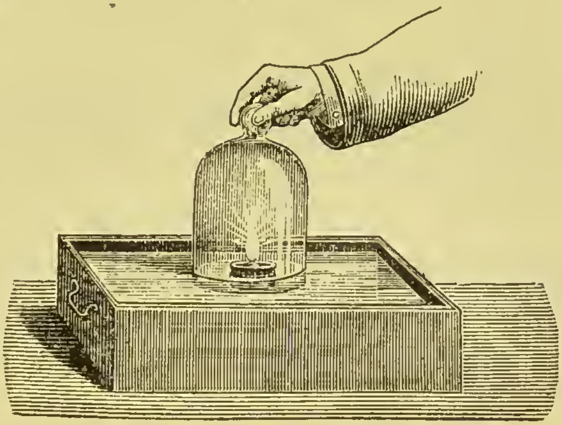
1. NITROGEN.

$N = 14.041.$ $N_2 = 28.082.$

Nitrogen exists free in the air, of which it constitutes $\frac{4}{5}$ and oxygen the remaining $\frac{1}{5}$. In combination, it is chiefly found in the ammonium and nitric acid compounds, as well as in many organic substances of the animal and vegetable kingdoms.

To isolate nitrogen from the air, the latter must be deprived of its second constituent. This is effected by such bodies as are capable of absorbing oxygen without acting upon the nitrogen. This is most readily brought about by the combustion of phosphorus. Several pieces of the latter are placed in a dish swimming on water, then ignited, and a glass bell jar placed over them (Fig. 62). In a short time, when all the oxygen is absorbed from the air, the phosphorus will cease burning; the phosphorus pentoxide produced dissolves in the water, and the residual gas consists of almost pure N: its volume will equal four-fifths of the air taken. Another procedure consists in conducting air through a red-hot tube filled with copper turnings; the copper unites with the oxygen and pure nitrogen escapes. At ordinary temperatures the removal of O from the air may be accomplished by the action of phosphorus, a solution of pyrogallic acid, and other substances.

FIG. 62.



A very convenient course for the direct preparation of nitrogen is the following: Heat ammonium nitrite in a small glass retort; this decomposes the salt directly into water and nitrogen:—

$$\underset{\text{Ammonium nitrite.}}{NH_4NO_2} = N_2 + 2H_2O.$$

In place of ammonium nitrite a mixture of potassium nitrite (KNO_2) and ammonium chloride (NH_4Cl) may be used; upon warming, these salts yield, by double decomposition, potassium chloride and ammonium nitrite ($KNO_2 + NH_4Cl = NH_4NO_2 + KCl$), which latter decomposes further. As potassium nitrite usually contains free alkali, some potassium bichromate is added to combine the same. Practically, the solution consists of 1 part potassium nitrite, 1 part ammonium chloride, and 1 part potassium bichromate, in 3 parts water, and is then boiled; to free the liberated nitrogen from every trace of oxygen the gas is conducted over ignited copper.

The action of chlorine upon aqueous ammonia produces nitrogen. The chlorine combines with the H of the ammonia, forming HCl, which unites with the excess of NH_3 to produce ammonium chloride.

The nitrogen that was in combination with the hydrogen is set free. The following equations express the reactions:—

$$2NH_3 + 3Cl_2 = N_2 + 6HCl,$$

and

$$6HCl + 6NH_3 = \underset{\text{Ammonium chloride.}}{6NH_4Cl}.$$

The apparatus pictured in Fig. 36, page 50, will serve to carry out the experiment. The disengaged chlorine is conducted through a Woulff wash bottle containing ammonia water, the free nitrogen being collected over water.

In this experiment the greatest care should be exercised that an excess of chlorine is not conducted into the solution, because its action upon the ammonium chloride will cause the formation of an exceedingly explosive body (nitrogen chloride, NCl_3, separating in oily drops).

Properties.—Nitrogen is a colorless, odorless, tasteless gas. Its density = 14.01 (H = 1) or 0.9701 (air = 1). Its critical temperature lies near —146°, and its critical pressure equals 33 atmospheres (p. 47). Liquid nitrogen is colorless, boils under a pressure of one atmosphere at —194°, at —225° under a pressure of 4 mm., and has a sp. gr. of 0.885 (at —194°). It solidifies at —214°. In its chemical deportment it is extremely inert, combining directly with only a few elements, and entering into chemical reaction but slowly. It does not support combustion or respiration; a burning candle is extinguished, and animals are suffocated by it. This is not due to the activity of the N, but to absence of O—a substance which cannot be dispensed with in combustion and respiration. The presence of N in the air moderates the strong oxidizing property of the pure oxygen.

THE ATMOSPHERE.

The air, or the envelope encircling the earth, consists principally of a mixture of nitrogen and oxygen; it always contains, in addition, slight and variable quantities of aqueous vapor, carbon dioxide and traces of other substances, as accidental constituents. The pressure exerted by the air is measured by a column of mercury which holds it in a state of equilibrium; the height of the barometric column at the sea level and 0° C. equals, upon an average, 760 millimeters. As 1 c.c. of mercury weighs 13.596 grams, 76 c.c. will equal 1033.7 grams, and the last number would indicate the pressure which the column of air exercises upon one square centimeter of the earth's surface.

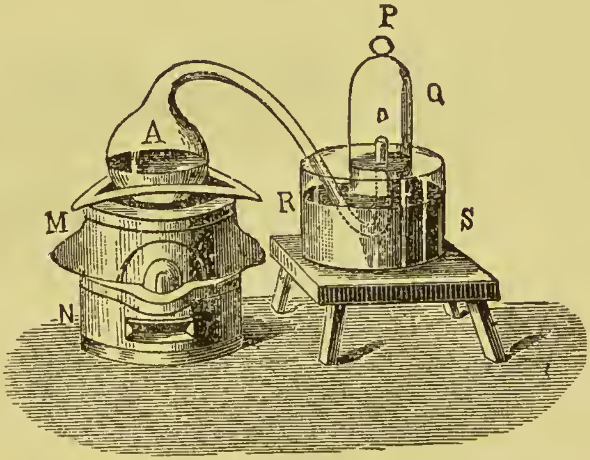
1 c.c. air weighs (at 0° C., and 760 mm. pressure) 0.00129318

grams; 1000 c.c., therefore, or one litre, would weigh 1.293 grams. As one litre of H_2O weighs 1000 grams, air is consequently 773 times lighter than it. Air is 14.43 times heavier than hydrogen. The specific gravities of the gases and vapors were formerly referred to air (= 1); compared with H = 1, they are, therefore, 14.43 times greater than before.

Remarks.—From these data, with the aid of the specific gravities derived from the molecular weights, the absolute weights of definite volumes of all gases may be readily determined, a problem frequently presented for solution in practice. One litre of air weighs 1.293 grams, one litre of hydrogen 0.08958 grams. To ascertain the weight of a litre of any other gas or vapor, its specific gravity referred to air = 1 must be multiplied by 1.293, or if compared with H = 1 by the factor 0.08958.

History.—In ancient times air, like fire and water, was regarded as an element. In the beginning of the seventeenth century it became known that by combustion and respiration in an enclosed space a portion of the air disappeared, and that the part remaining was no longer suitable for the support of the above processes; hence this was called *destroyed air;* and the first, *fire air.* In the second half of the eighteenth century Scheele, in Sweden, and Priestley, in England, found that when a certain amount of gas, set free by heating mercuric oxide (oxygen), was added to the so-called *destroyed air* (nitrogen) a mixture resulted possessing all the properties of atmospheric air. Although both constituents of air were thus separately obtained and air regenerated by their mixture, yet at that time views regarding the nature of both ingredients and the nature of combustion and oxidation processes prevailed which were perfectly false in every respect. It was believed that combustion and oxidation were destructive processes; that the combustible and oxidizable bodies enclosed within themselves a peculiar substance called *phlogiston.* The latter was said to escape as fire and heat (phlogiston theory of Stahl, 1723), in the processes of combustion and reduction. These erroneous opinions were explained and corrected by Lavoisier (in 1774) by the following celebrated experiment bearing upon the composition of the air: A glass sphere, provided with a long, twice bent neck (Fig. 63), was filled with a weighed quantity of mercury. The open end of the neck dipped into a mercury trough, *R S*, and was closed completely by a glass bell jar. Then the balloon *A* was heated for some days at a temperature near the boiling point of mercury. By this means the mercury absorbed the oxygen of the air contained in *A* and the bell jar *P*, forming mercuric oxide. In the course of several days, during which no additional decrease in the volume of air was observable on the application of heat, the

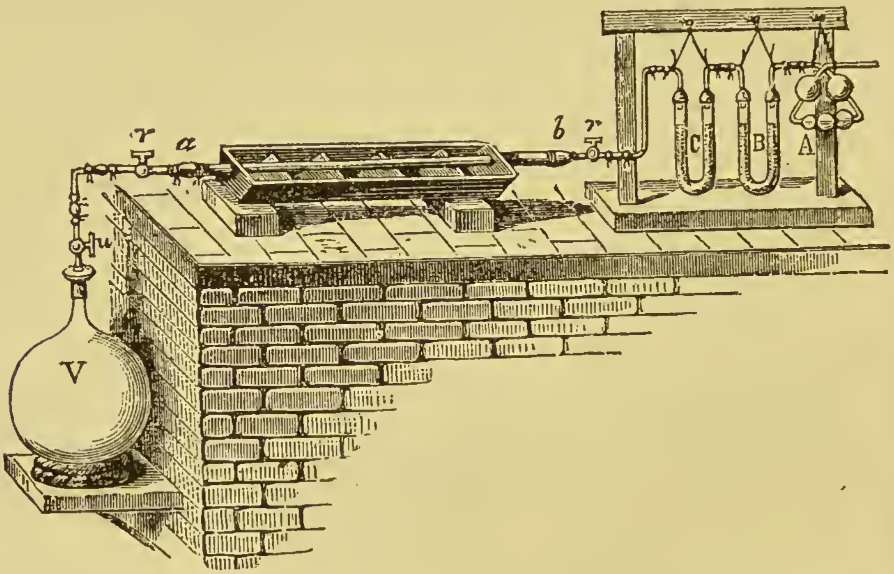
FIG. 63.



experiment was interrupted and the volume of residual gas in *A* and *P* measured. Upon comparing this with the volume before the experiment, it was discovered that $\frac{1}{5}$ volume of the air had disappeared and combined with the mercury to form red mercuric oxide. Lavoisier now strongly ignited the resulting mercuric oxide, and obtained a volume of oxygen equal to that withdrawn from the air during the experiment. By mixing this with the residual volume of N the original volume of air was again recovered. Thus it was demonstrated that air consists of $\frac{4}{5}$ volumes N and $\frac{1}{5}$ volume O gas. The elementary character of nitrogen was first established by Lavoisier in 1787. It was called azote (from ζώη, life, and ἀ, privative) by him. The symbol *Az*, derived from azote, is used in France and England for nitrogen. The name nitrogenium (from which the symbol N) was given to nitrogen because it was a constituent of saltpetre (nitrum).

Lavoisier made use of the above experiment for another important deduction. As he determined the weight, both of the employed mercury and the resulting mercuric oxide, he discovered that the increase in weight was exactly equal to that of the oxygen withdrawn from the air, and by heating the mercuric oxide the same weight of oxygen was again separated. Thus was it demonstrated that the process of oxidation was the union of two bodies (not a decomposition), and that the weight of a compound body equals the sum of the weights of its constituents; the principle of the indestructibility of matter.

Fig. 64.



Quantitative Composition of Air.—Its composition is expressed by the quantity of oxygen and nitrogen contained in it, as its remaining admixtures are more or less accidental and variable. Boussingault and Dumas determined the accurate weight composition of the air by the following experiment: A large balloon, *V*, with a capacity of about 20 litres (Fig. 64), is connected with a porcelain tube, *a b*, filled with metallic copper. Balloon and tubes, closed by stop-cocks, are previously emptied and weighed apart. The bent tubes, *A*, *B*, and *C*, contain KOH and sulphuric acid, and serve to free the air undergoing analysis from aqueous vapor, carbon dioxide, and other impurities. The porcelain tube, filled with copper, is heated to a red heat, and by carefully opening the stop-cocks *u*, *r*, and *r′* a slow current of air is allowed to enter the empty balloon *V*. The impurities are given up in the bent tubes, and all the oxygen absorbed by the ignited Cu, forming cupric oxide, so that only pure nitrogen enters *V*. Now close the cocks and weigh the balloon and porcelain tube. The increase in weight of the latter represents the quantity of oxygen in the air; the increase in *V* the quantity of *nitrogen*. In this manner Dumas and Boussingault found that in 100 parts by weight of air there are contained :—

Nitrogen	76.99	parts by weight.
Oxygen	23.01	" " "
	100.00	" " "

As we know the specific gravity of nitrogen (14.01) and of oxygen (15.96), we can readily calculate the volume composition of air from that in parts by weight. We thus discover: —

Oxygen	20.78	parts by volume.
Nitrogen	79.22	" " "
Air	100.00	" " "

Calculating upon these numbers, we obtain 14.415 ($H = 1, O = 15.96$) as the specific gravity of air.

The volume composition of air may be directly found by means of the absorptiometer. The latter is a tube carefully graduated, and sealed at one end. This is filled with mercury, and air allowed to enter; the volume of the latter is determined by reading off the divisions on the tube. Now introduce into the tube, through the mercury, a platinum wire having a ball of phosphorus attached to the end (Fig. 65), (or a ball of coke saturated with an alkaline solution of pyrogallic acid). The phosphorus absorbs the oxygen of the air, and only nitrogen remains, the volume of which is read off by the graduation.

The *eudiometric method* affords greater accuracy. It is dependent upon the combustion of the oxygen with hydrogen in a eudiometer. The latter is an absorptiometer, having two platinum wires fused in its upper end (Fig. 66). Air and hydrogen are introduced into the eudiometer, and the electric spark then passed through the wires (Fig. 67). All the oxygen in the air combines with a portion of the hydrogen to form water. On cooling, the aqueous vapor condenses and a contraction in volume occurs. Assuming that we had taken 100 volumes of air and 50 volumes of hydrogen, and that the residual volume of gas, after allowing for all corrections (p. 123), equalled 87.15; then of the original 150 volumes of mixed gas, 62.85 volumes disappeared in the formation of water. As the latter results from the union of 1 volume of oxygen and 2 volumes of hydrogen, the 100 volumes of air employed in the analysis therefore contained $\frac{62.85}{3} = 20.95$ volumes of oxygen. From this air consists of

FIG. 65.

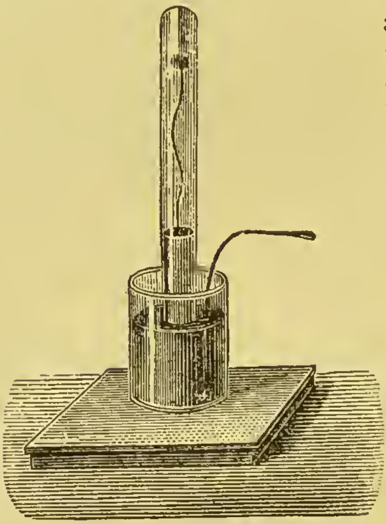
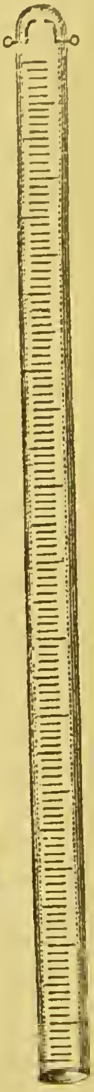


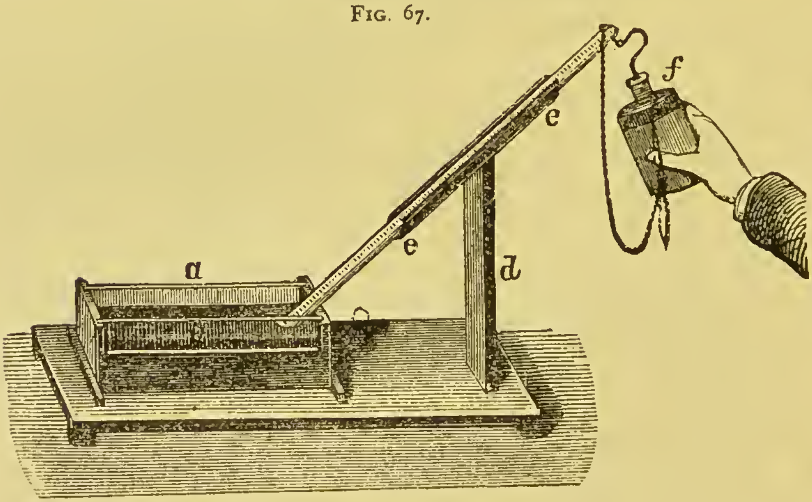
FIG. 66.



79.05 volumes nitrogen.
20.95 " oxygen.
100.00 " air.

Numerous analyses show that the composition of the air everywhere on the earth's surface is constant. The opinion was long held that variations in composition equaling 0.5 per cent. existed at various periods of the year and in various localities. The recent extended investigations of Kreusler and Hempel prove these assumptions to have been based upon erroneous

FIG. 67.



determinations. The oxygen content of the air varies constantly from 20-91 to 20-93 per cent. by volume.

Measuring Gases.—The volume of gases is influenced by pressure, temperature, and the moisture contained in them. The volume of dry gases, at 760 mm. barometric pressure and 0° C., is accepted as the normal volume. If a gas has been measured under any other conditions it must be reduced to the normal volume. According to the law of Boyle and Mariotte, the volumes of the gases are inversely proportional to the pressure; therefore, if the volume of the gas at pressure h, has been found equal to V, its volume at 760 mm. equals $\frac{Vh}{760}$.

According to Gay-Lussac's law, all gases expand in proportion to the temperature. Their coefficient of expansion is $\frac{1}{273} = 0.003665$; *i. e.*, one volume of gas at 0° occupies at 1° the volume 1.003665. If V_t represents the observed gas volume at $t°$, V_0, however, its volume at 0°, then

$$V_0 = \frac{V_t}{1 + 0.003665.t}\text{*},$$

and, considering the pressure,

$$V_0 = \frac{V_t h}{760(1 + 0.003665.t)}.$$

Further, the gas volume is enlarged by moisture, as the tension of the aqueous vapor opposes the atmospheric pressure. The moisture may be removed by introducing into the gas a ball of coke saturated with sulphuric acid, which dries it. It is more convenient, however, to make the correction of the gas volume in the following manner: Water is brought in contact with the gas to be measured, in order to perfectly saturate it with aqueous vapor; the gas is then measured and its normal volume calculated by the above formula, after deducting from the observed pressure h the number of millimeters corresponding to the tension of the aqueous vapor for the given temperature (p. 91).

From the great constancy of its composition air was supposed to be a chemical compound, consisting of nitrogen and oxygen. This supposition is, however, opposed by the following circumstances. All chemical compounds contain their constituents in atomic quantities, which is not the case with air. In the mixing of nitrogen and oxygen to form air there is neither disengagement nor absorption of heat, which is always observed in chemical compounds. Further, the air absorbed by water or other solvents possesses a composition different from the atmospheric; this is due to the unequal solubilities of nitrogen and oxygen in water. The air expelled from water upon application of heat consists of 34.9 volumes of oxygen and 65.1 volumes nitrogen. (Bunsen.) These facts indicate that air is not a chemical compound, but a mechanical mixture of its two constituents.

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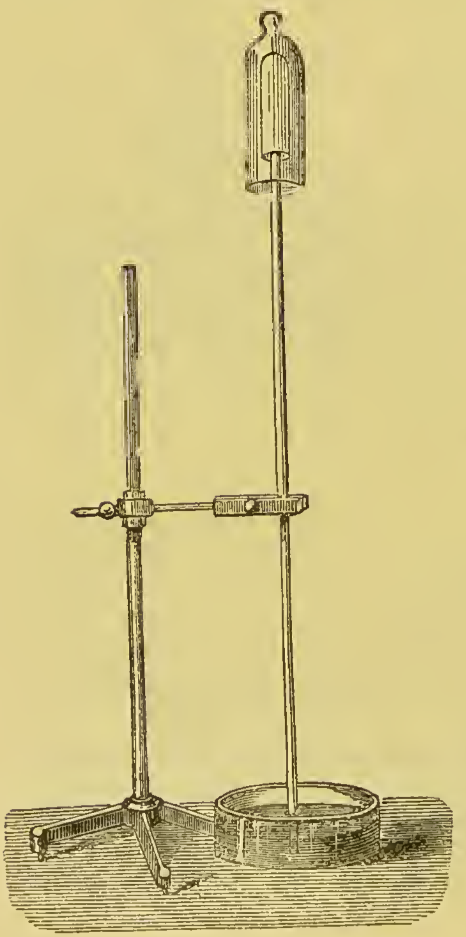
* $V_0 = V_t - V_0 .0.00366.t$, consequently $V_0 + V_0 .0.00366.t = V_t$, and $V_0 (1 + 0.00366.t) = V_t$.

The great constancy in composition of the air depends on the mutual diffusion of the gases. As the gas molecules possess a direct progressive movement, they distribute themselves, without limitation, into space, and intermingle regularly with each other. *The velocity of the diffusion of gases is approximately inversely proportional to the square root of their densities*—the law of the diffusion of gases. The density of hydrogen = 1; the density of oxygen = 16; therefore, hydrogen diffuses 4 times more rapidly than oxygen. The unequal diffusion of gases may be perceived if they are allowed to pass through very narrow apertures, or through porous partitions. The following experiment very clearly illustrates this: In the open end of an unglazed clay cylinder (as used in galvanic elements) there is puttied a glass tube about one meter long, its open end terminating in a dish containing water (Fig. 68); the cylinder and tube are filled with air. Over the porous cylinder is placed a wider vessel filled with hydrogen. The latter presses almost four times faster into the cylinder than the air escapes from it; the air in the tube and cylinder is displaced and rises in the water in bubbles. When the separation of gas ceases, tube and cylinder are almost filled with pure hydrogen. On removing the larger hydrogen vessel the gas will escape much more rapidly into the external air than the latter can enter the cylinder; the internal pressure will therefore be less than the external, and water ascends in the glass tube.

FIG. 68.



In addition to N and O, air constantly contains aqueous vapor and carbon dioxide in very small quantities. The presence of the former can readily be recognized by the fact that cold bodies are covered with dew in moist air. Its quantity depends on the temperature and corresponds to the vapor tension of water (see p. 91). 1 cubic meter of air perfectly saturated with aqueous vapor contains 22.5 grams water at 25° C.; on cooling to 0° 17.1 grams of these separate as rain. Generally the air contains only 50–70 per cent. of the quantity of vapor necessary for complete saturation. The amount of moisture in it is either determined according to physical methods (hygrometer), or directly by weighing. To this end a definite quantity of air is conducted through a tube filled with calcium chloride or sulphuric acid, and its increase in weight determined.

To detect the carbon dioxide in the air, conduct a portion of the latter through solutions of barium or calcium hydroxides, and a turbidity will ensue. To determine its quantity, pass a definite and previously dried amount of air through a weighed potassium hydrate tube, and ascertain the increase in weight of the latter. 10,000 parts of atmospheric air contain, ordinarily, from 2.9–3.0 parts carbon dioxide.

Besides the four ingredients just mentioned, air usually contains small quantities of ozone, hydrogen peroxide, and ammonium salts (ammonium nitrite). Finally, air contains microscopic germs of lower organisms; they are generally found in the lower air strata, and their presence influences the processes of the decay and fermentation of organic substances.

COMPOUNDS OF NITROGEN WITH HYDROGEN.

AMMONIA.

$NH_3 = 17.04$. Density $= 8.52$.

Ammonia occurs in the air in combination with some acids, in natural waters and in the earth, but always in small quantities. The formation of ammonia by the direct union of nitrogen and hydrogen occurs under the influence of the silent electric discharge. Its compounds are frequently produced under the most varying conditions. Thus ammonium nitrate is formed by the action of the electric spark upon moist air:—

$$N_2 + O + 2H_2O = \underset{\text{Ammonium nitrate.}}{NH_4NO_3}.$$

Small quantities of ammonium nitrite result by the evaporation of water in the air:—

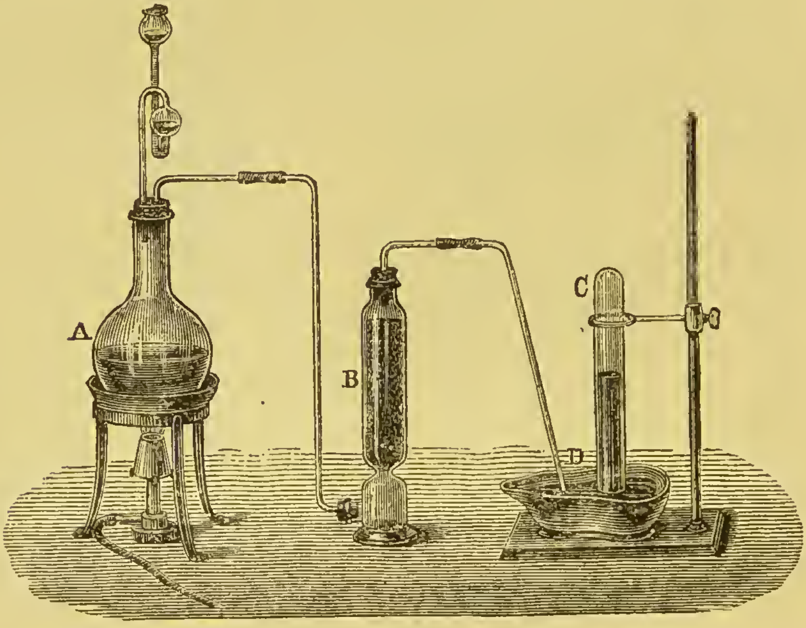
$$N_2 + 2H_2O = \underset{\text{Ammonium nitrite.}}{NH_4NO_2}.$$

The same salt is formed in every combustion in the air; by the rusting of iron and in the electrolysis of water. The white vapors which moist phosphorus forms in the air, consist of ammonium nitrite. Further, ammonium salts are produced in the solution of many metals in nitric acid, in consequence of a reduction of the acid by the liberated hydrogen:—

$$HNO_3 + 4H_2 = 3H_2O + NH_3.$$

Ammonia is produced in large quantities in the decomposition and dry distillation of nitrogenous organic substances. Even as late as the last century the bulk of the ammonium chloride (the most important salt technically), was obtained by the distillation of camel's dung (in Egypt in the oasis of Jupiter Ammon—hence the name *Sal ammoniacum*). In the preparation of illuminating gas by the distillation of coal, ammonia appears as a by-product and may be obtained by combining it with sulphuric or hydrochloric acid. This method is used almost exclusively at present for its production.

FIG. 69.



To prepare ammonia heat a mixture of ammonium chloride and slaked lime in a glass or iron flask:—

$$\underset{\substack{\text{Ammonium}\\ \text{chloride.}}}{2NH_4Cl} + \underset{\substack{\text{Calcium}\\ \text{hydroxide.}}}{Ca(OH)_2} = CaCl_2 + 2H_2O + 2NH_3.$$

The disengaged ammonia gas is collected over mercury, as it is readily soluble in water (Fig. 69). For perfect drying conduct it through a vessel filled with burnt lime (CaO). Calcium chloride is not applicable for this purpose, as it combines with the gas. In consequence of its levity, ammonia, like hydrogen, may be collected by displacing the air in inverted vessels.

Physical Properties.—Ammonia is a colorless gas with a suffocating characteristic odor. Its density is 8.5 (H = 1), or 0.589 (air = 1). Under a pressure of 6.5 atmospheres (at 10° C.), or by cooling to

—40° C., it condenses to a colorless, mobile liquid with a specific gravity of 0.613 at 0°, and solidifies at —80°.

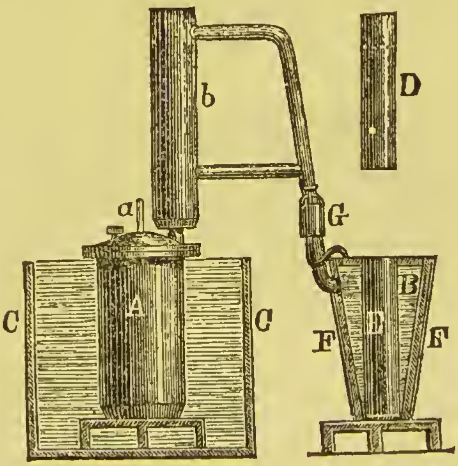
Ammonia gas may be condensed, just like chlorine. Take ammonium silver chloride ($AgCl.2NH_3$), obtained by conducting ammonia over silver chloride, and enclose it in a tube with a knee-shaped bend (Fig. 70). The limb containing the compound is now heated in a water-bath, while the other limb is cooled. The compound is decomposed into silver chloride and ammonia, which condenses in the cooled limb.

Fig. 70.

Ammonia gas dissolves very readily in water, with the liberation of heat. One part of water at 0° and 760 mm. pressure absorbs 1050 volumes (= 0.877 parts by weight); at 15°, 730 volumes of ammonia. When a long glass tube, closed at one end and filled with ammonia, has its open end placed in water, the latter rushes up into the tube as it would into a vacuum; a piece of ice melts rapidly in the gas. The aqueous solution possesses all the properties of the free gas, and is called *Liquor ammonii caustici.* The greater the ammonia content the less will the specific gravity of the solution be. The solution saturated at 40° contains about 30 per cent. NH_3, and has a specific gravity of 0.897. All the gas escapes on the application of heat.

When the condensed liquid ammonia evaporates it absorbs a great amount of heat, and answers, therefore, for the production artificially of cold and ice in Carrè's apparatus. The simplest form of the latter is represented in Fig. 71. The iron cylinder *A* is filled about half with a concentrated aqueous ammonia solution, and is connected, by means of the tubes from *b*, with the conical vessel *F*, in the middle of which is the empty cylindrical space *E*. The entire internal space of *A* and *F* is hermetically shut off. *A* is heated upon a charcoal fire until the thermometer *a*, in it, indicates 130° C., while *F* is cooled with water. In this way the gaseous ammonia is expelled from the aqueous solution in *A*, passes through *b*, in which most of the water runs back, and condenses to a liquid in *B*, of the receiver *F*. The cylinder *A* is removed from the fire, cooled with water and the vessel *D* constructed of thin sheet-metal and filled with water, placed in the cavity *E*, which is surrounded with a poor conductor, *e. g.*, felt. The ammonia condensed in *B* evaporates, and is reabsorbed by the water in *A*. By this evapo-

Fig. 71.



ration a large quantity of heat, withdrawn from *F* and its surroundings, becomes latent; the water in *D* freezes.

The method of Carrè for the artificial production of ice has acquired great application in the arts; recently, however, it has been more and more replaced by the method of Windhausen. The latter depends upon the expansion of compressed air.

Chemical Properties.—A red heat and continued action of the electric spark decompose ammonia into nitrogen and hydrogen. On conducting ammonia gas over heated sodium or potassium, the nitrogen combines with these metals and hydrogen escapes:—

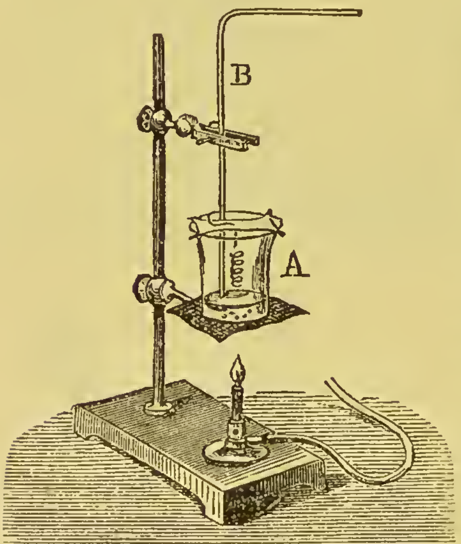
$$NH_3 + 3K = NK_3 + 3H.$$

Ammonia will not burn in the air; in oxygen, however, it burns with a yellow flame:—

$$2NH_3 + 3O = N_2 + 3H_2O;$$

ammonium nitrite and nitrogen dioxide are formed simultaneously. When a mixture of ammonia and oxygen is ignited it burns with explosion.

Fig. 72.



To show the combustion of NH_3 in O, proceed as follows: A glass tube, through which ammonia is conducted, is brought into a vessel with oxygen, bringing the opening of the latter near a flame at the moment of the introduction of the glass tube. In contact with oxygen, the ammonia gas ignites and continues to burn in it.

The following experiment (of Kraut) shows the combustion of ammonia very conveniently. Place a somewhat concentrated ammonia solution in a beaker glass; heat over a lamp, until there is an abundant disengagement of gas, and then run in oxygen gas, by means of a tube dipping into the liquid. Upon approaching the mixture with a flame, it ignites with a slight explosion. The ignition may be induced without a flame, by sinking a glowing platinum spiral into the mixture (Fig. 72); we then have a number of slight explosions. The glass is filled at the same time with white vapors of ammonium nitrite (NH_4NO_2); later, when oxygen predominates, red vapors of nitrogen dioxide (NO_2) and nitrous acid appear.

If chlorine gas be conducted into the vessel with ammonia, it immediately ignites and continues to burn in the latter, with the production of white fumes of ammonium chloride (NH_4Cl). The chlorine combines with the hydrogen of the ammonia, with separation of nitrogen, and yields hydrochloric acid, which unites to form ammonium chloride with the excess of ammonia.

$$NH_3 + 3Cl = 3HCl + N,$$
$$\text{and } 3NH_3 + 3HCl = 3NH_4Cl.$$

Chlorine reacts similarly upon aqueous ammonia (p. 118).

In gaseous form, as well as in solution, ammonia possesses strong basic properties; it blues red litmus paper, neutralizes acids, forming salt-like compounds with them, which are very similar to the salts of the alkalies—sodium and potassium. The following illustrates the similarity:—

NH_3	+	HCl	=	NH_4Cl	KCl
				Ammonium chloride.	Potassium chloride.
$2NH_3$	+	H_2SO_4	=	$(NH_4)_2SO_4$	K_2SO_4
				Am. sulphate.	Potassium sulphate.
NH_3	+	H_2S	=	NH_4SH	KSH.
				Am. sulphydrate.	Potassium sulphydrate.

In these ammonia derivatives NH_4 plays the rôle of the metal potassium. Hence the group (NH_4) has been designated *Ammonium* and its compounds, *ammonium salts*. The latter, when acted on by strong bases, yield ammonia gas:—

$$2NH_4Cl + CaO = 2NH_3 + CaCl_2 + H_2O.$$

The metallic character of the ammonium group is confirmed by the existence of the ammonium amalgam, and likewise by its entire deportment in compounds. Therefore, the ammonium derivatives will be considered with the metals.

Thermo-chemical Deportment.—The heat of formation of ammonia from hydrogen and nitrogen equals 11.8 Cal. When ammonia gas is dissolved in much water 8.8 Cal. are set free, so that the heat of formation of ammonia from its elements in dilute aqueous solution equals 20.6 Cal.:—

$$(N,H_3 - \text{gas}) = 11.8. \quad (NH_3,Aq) = 8.8. \quad (N,H_3,Aq) = 20.6.$$

Although an exothermic compound, ammonia is produced from its elements with difficulty, and in turn is rather easily dissociated into them. The rather great heat of solution of gaseous ammonia explains why ice will melt in the same (p. 127).

The explosibility of a mixture of ammonia and oxygen is accounted for by the following large heat disengagement:—

$$\underset{(23.6 \text{ Cal.})}{2NH_3} + 3O = \underset{(3 \times 57.2 \text{ Cal.})}{3H_2O} + N_2 \quad . \quad . \quad . \quad . \quad (+ 148.0 \text{ Cal.})$$

The action of chlorine upon gaseous or aqueous ammonia is also very energetic:—

$$\underset{(11.8 \text{ Cal.})}{NH_3 \text{ gas}} + 3Cl = \underset{(66 \text{ Cal.})}{3HCl \text{ gas}} + N \quad . \quad . \quad . \quad . \quad (+ 54.2 \text{ Cal.})$$

$$\underset{(20.6 \text{ Cal.})}{NH_3\text{-dissolved}} + 3Cl = \underset{(3 \times 39.3 \text{ Cal.})}{3HCl\text{-dissolved}} + N \quad . \quad . \quad . \quad (+ 97.3 \text{ Cal.})$$

When there is an excess of ammonia the hydrochloric acid combines with it to form ammonium chloride ($NH_3 + HCl = NH_4Cl$), and in doing this both the heat disengagement and the energy of reaction are raised still further.

QUANTITATIVE COMPOSITION OF AMMONIA. ATOMIC WEIGHT OF NITROGEN.

The quantitative analysis of ammonia shows that it consists of 1 part hydrogen and 4.67 parts nitrogen; hence we conclude that the atomic weight of N is a multiple of the last number (see p. 98):—

$$\begin{array}{lcl} H & = & 1 \\ N & = & 4.67 \\ \hline NH & = & 5.67 \end{array} \qquad \begin{array}{lcl} 2H & = & 2 \\ N & = & 9.34 \\ \hline NH_2 & = & 11.34 \end{array} \qquad \begin{array}{lcl} 3H & = & 3 \\ N & = & 14.04 \\ \hline NH_3 & = & 17.04 \end{array}$$

As the density of ammonia equals 8.5 ($H = 1$), its molecular weight would almost $= 17$. In 17.04 parts of ammonia there are 3 parts, and, therefore, 3 atoms of hydrogen. That the 14.04 parts nitrogen united with them correspond to *one* atom of N is a consequence, as never less than 14.04 parts of N are present in the molecular weight of any nitrogen derivative. The density of nitrogen equals 14.04, and its molecular weight 28.08; therefore, the molecule of N consists of two atoms (N_2). This is also concluded from the volume ratios occurring in the formation of ammonia. (See below.)

From the molecular formulas NH_3 and N_2 it follows, further, that 1 volume N and 3 volumes H form 2 volumes ammonia gas, or that 2 volumes NH_3 decompose into 3 volumes H_2 and 1 volume N_2, corresponding to the molecular equation:—

$$\underset{1 \text{ vol.}}{N_2} + \underset{3 \text{ vols.}}{3H_2} = \underset{2 \text{ vols.}}{2NH_3}.$$

The following experiments prove these conclusions:—

1. Decompose an aqueous ammonia solution, mixed with sulphuric

acid to increase its power of conductivity, in a Hofmann's apparatus (Fig. 47), by the galvanic current. Hydrogen will separate at the negative and nitrogen at the positive pole; the former will have three times the volume of the latter.

2. The electric (induction) sparks are permitted to strike through dry ammonia gas enclosed in a eudiometer, or the apparatus represented in Fig. 58. In this way the ammonia is decomposed into nitrogen and hydrogen, whose volume is twice as large as that of the ammonia employed. That 3 vols. H are present in the mixture for every vol. N is easily shown by the volumetric method, by burning the H with oxygen (p. 121).

The volume ratios in the formation of ammonia confirm the conclusion drawn from the density of nitrogen (see above), that the molecule of the latter consists of two atoms. In two volumes of ammonia there are 2*n* molecules of NH_3, therefore 2*n* atoms of N. The nitrogen contained in these 2 volumes of NH_3 occupies 1 volume in a free condition, and this contains *n* molecules and therefore 2*n* atoms of N.

HYDROXYLAMINE.

$NH_3O = NH_2OH$.

This compound, very analogous to ammonia, was discovered (by Lossen) in the reduction of ethyl nitrate by tin and hydrochloric acid. It is produced, too, by the action of tin upon dilute nitric acid, and by tin and hydrochloric acid upon all the oxygen compounds of nitrogen. In all these reactions it is the hydrogen eliminated by the tin which, in *statu nascendi*, reduces the nitric acid:—

$$HNO_3 + 3H_2 = H_3NO + 2H_2O.$$

To prepare hydroxylamine treat ethyl nitrate (120 gr.) with granulated tin (400 gr.) and hydrochloric acid (800–1000 c.c. of specific gravity 1.19, mixed with three times its volume of water) until solution is obtained. The strongly concentrated liquid is cooled and supersaturated with soda, the filtrate slightly acidulated with hydrochloric acid and then evaporated to dryness. Hot alcohol will extract hydroxylamine hydrochloride, $NH_3O.HCl$, from the residue.

Hydroxylamine hydrochloride is most easily formed by acting with hydrochloric acid upon fulminating mercury (see Organic Chemistry).

Hydroxylamine is very similar to ammonia, and like it unites directly with the acids to form salts:—

$$H_3NO + HCl = H_3NO.HCl.$$

The hydrochloride in distinction to ammonium chloride is perfectly insoluble in absolute alcohol. It passes into ammonium chloride when allowed to stand exposed to the air.

On adding to the aqueous solution of the sulphate of hydroxylamine sufficient barium hydroxide to remove all the sulphuric acid, an aqueous solution is obtained, which, like the ammonia solution, possesses strong basic properties, and blues red litmus paper. The solution is, however, very unstable, and readily decomposes into water, ammonia, and nitrogen :—

$$3NH_3O = NH_3 + 3H_2O + N_2.$$

Upon the application of heat a portion of the hydroxylamine will be carried over undecomposed along with the steam, but most of it is broken up. The hydroxylamine solution manifests a reducing action ; it precipitates metallic silver from silver nitrate, white mercurous chloride, $HgCl$, from mercuric chloride, $HgCl_2$, and cuprous oxide from cupric salts.

Owing to its great similarity to ammonia and its various reactions, it is supposed that hydroxylamine represents ammonia in which 1 H is replaced by the hydroxyl group OH ; therefore the name hydroxylamine :—

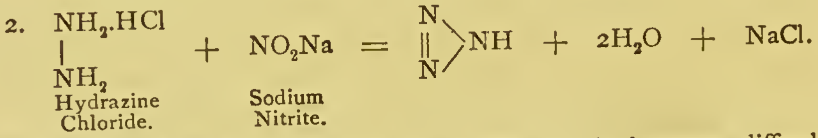
$$NH_3O = NH_2OH.$$

Diamide or *Hydrazine*, $N_2H_4 = H_2N.NH_2$, a compound of two amido-groups (NH_2), was until recently only known in its numerous organic derivatives. Curtius has at last succeeded in isolating it. Its salts, *e. g.*, $N_2H_4.2HCl$, result from the transposition of a complex diazofatty acid. Alkalies liberate the free diamide from the latter. It is a stable gas with peculiar odor. It is very similar to ammonia, dissolves easily in water, colors red litmus blue and combines with the acids (2 equiv.) to form salts. One of its characteristic reactions is the reduction of silver and copper salts.

Its salts will be described under the metals as diamide or diammonium salts.

Hydrazoic Acid, HN_3, Azoimide, is an interesting derivative of hydrazine. It is formed under proper conditions by the action of nitrous acid upon diamide. Ammonia and nitrous acid yield nitrogen, and hydrazine monochloride and nitrites should form hydrazoic acid :—

$$1.\quad \underset{\text{Ammonium Chloride.}}{NH_4Cl} + \underset{\text{Sodium Nitrite.}}{NO_2Na} = N_2 + 2H_2O + NaCl.$$



$$2.\quad \underset{\text{Hydrazine Chloride.}}{\begin{matrix}NH_2.HCl\\ |\\ NH_2\end{matrix}} + \underset{\text{Sodium Nitrite.}}{NO_2Na} = \begin{matrix}N\\ \|\\ N\end{matrix}\!\!>NH + 2H_2O + NaCl.$$

The direct preparation of the acid from hydrazine is, however, difficult. An easy method for its preparation consists in acting upon hippuryl hydrazine $(C_9H_8O_2).NH.NH_2$, with sodium nitrite and acetic acid. The product is boiled with acids or alkalies, when the resulting hydrazoic acid is carried over with steam.

At the ordinary temperature hydrazoic acid is a gas, producing dizziness, headache, and inflammation of the membrane of the nasal cavity. Its aqueous solution has a penetrating odor. Blue litmus, held over the liquid, is colored an intense red. Its vapors form dense clouds with ammonia. A 70 per cent. solution of the acid dissolves iron, zinc, copper, aluminium and magnesium energetically. In concentrated form it appears to dissolve gold and silver. Its metallic salts are very similar to the chlorides. The acid itself is distinguished from the haloid acids by its extremely explosive character. Silver nitrate and mercurous nitrate precipitate it quantitatively from its solutions. Silver hydrazoide, AgN_3, is extremely like silver chloride, but is not changed on exposure to the light. (*Berichte*, 23, 3023).

COMPOUNDS OF NITROGEN WITH THE HALOGENS.

NITROGEN CHLORIDE.

NCl_3.

As we have seen, nitrogen is liberated when chlorine acts upon an excess of ammonia (p. 129); when, however, the chlorine is in excess, it acts upon the previously formed ammonium chloride, to produce nitrogen chloride:—

$$NH_4Cl + 3Cl_2 = NCl_3 + 4HCl.$$

For the preparation of a small quantity of nitrogen chloride, dip a flask filled with chlorine, open end down, into an aqueous ammonium chloride solution, warmed to 30°. The chlorine is absorbed, and heavy oil drops separate, which are best collected in a small leaden dish.

Nitrogen chloride is an oily, yellow liquid, with a disagreeable odor; its specific gravity equals 1.65. Of all chemical compounds this is the most dangerous, as it decomposes by the slightest contact with many substances, and frequently, too, without any perceptible external cause. Its decomposition is accompanied by an extremely violent report. Aqueous ammonia gradually decomposes it into ammonium chloride and nitrogen:—

$$NCl_3 + 4NH_3 = 3NH_4Cl + N_2.$$

It is converted into ammonium chloride and free chlorine by concentrated hydrochloric acid:—

$$NCl_3 + 4HCl = NH_4Cl + 3Cl_2.$$

This reaction is directly opposed to that by which nitrogen chloride is formed.

The formation and explosibility of nitrogen chloride may be illustrated in a harmless way as follows: Decompose a saturated ammonium chloride solution with the electric current. Nitrogen chloride rising in small drops from the liquid will separate at the positive pole. Upon covering the surface of the solution with a thin layer of turpentine oil, each drop will explode as it comes in contact with the latter.

Nitrogen Iodide. Upon adding ammonium hydroxide, or a mixture of ammonium chloride and caustic soda, to a solution of iodine in aqueous potassium iodide, a brownish black powder separates. Its composition closely approximates the formula, NI_2H. Its formation by means of ammonium chloride and caustic soda is represented in the equation:—

$$4I + NH_4Cl + 3NaOH = NI_2H + 3H_2O + NaCl + 2NaI.$$

When the conditions are slightly changed a very similar compound separates. Its formula is $N_2I_3H_3(= NH_3 + NI_3)$. Protracted washing with water decomposes it into ammonia and nitrogen tri-iodide, NI_3.

Nitrogen Di-iodide and **Nitrogen Tri-iodide,** NHI_2 and NI_3, are, when dry, very explosive. The explosibility may be shown without danger in the following manner: The precipitate is collected on a filter, washed with water, the filter opened out and torn into small pieces, which are then allowed to dry; upon the slightest disturbance these pieces explode with a sharp report.

Nitrogen iodide dissolves in dilute hydrochloric acid and decomposes into ammonia and iodine chloride:—

$$NH_2I + HCl = NH_3 + ICl.$$

Hydrogen sulphide and sulphurous acid convert it into ammonia and hydrogen iodide.

The nitrogen iodide formed by digesting powdered iodine with ammonia water manifests properties that are slightly different from those of the ordinary iodide. It is only stable in the presence of ammonia. It sometimes explodes even when moist—if it be washed with water, or when acted upon by hydrochloric acid.

Thermo-chemical Deportment.—Nitrogen chloride and iodide are both strongly endothermic compounds; considerable heat is absorbed in their production from the elements:—

$$(N,Cl_3) = -38.1 \text{ Cal.}$$

This being the case, they can only be obtained from their constituents by the addition of energy from without. Yet this formation does not occur, because the slightest external impulse occasions their decomposition. When they are formed from ammonium chloride by the action of chlorine (iodine) it is at the expense of the total heat of transposition, which continues positive:—

$$\underset{(75.8\text{ Cal.})}{NH_4Cl} + 6Cl = \underset{(-38.1\text{ Cal.})}{NCl_3} + \underset{(4 \times 39.3\text{ Cal.})}{4HCl\,Aq.} \;.\;.\;.\; + (81.4\text{ Cal.})$$

Inasmuch as these compounds contain a great deal more energy than their elements, they exist in a very uncertain equilibrium, and may be readily decomposed with explosion—they are very explosive (see p. 29).

2. PHOSPHORUS.

$P = 31.03$. $P_4 = 124.12$. Density $= 62.06$.

This element does not occur free in nature, because of its very great affinity for oxygen. The phosphates, especially calcium phosphate, are widely distributed. By the disintegration of the minerals containing phosphates the latter pass into the soil, are absorbed by plants, and remain in their ash. In the animal kingdom calcium phosphate occurs in the bones.

Brand and Kunkel, in Hamburg (1669), first obtained phosphorus by the ignition of evaporated urine. In 1769, Scheele, in Sweden, showed that it could be obtained from bones. Its name is derived from its power of giving light in the dark—*φωσφόρος*, *i. e*, light-bearer.

To obtain phosphorus from bones the latter are burned, thereby destroying all organic admixtures and leaving bone ashes, which consist principally of tertiary calcium phosphate $(PO_4)_2Ca_3$ (see Phosphoric Acid). The ashes are digested with ⅔ of their weight of sulphuric acid, when the tri-phosphate becomes primary calcium phosphate, and gypsum (cal. sulphate) is produced:—

$$\underset{\text{Tertiary calcium phosphate.}}{Ca_3(PO_4)_2} + 2H_2SO_4 = \underset{\text{Primary calc. phosphate.}}{CaH_4(PO_4)_2} + \underset{\text{Calcium sulphate.}}{2CaSO_4}.$$

The gypsum, which dissolves with difficulty in water, is separated from the readily soluble primary phosphate by filtration; the solution is mixed with charcoal, evaporated in leaden pans, and the residue raised to a red heat. This expels water from the primary phosphate and the latter changes to calcium metaphosphate:—

$$CaH_4(PO_4)_2 = \underset{\text{Calcium metaphosphate.}}{Ca(PO_3)_2} + 2H_2O.$$

The ignited residue is then raised to a white heat, in retorts of infusible clay. The carbon partly reduces the metaphosphate to phosphorus, by forming carbon monoxide with oxygen, and half of the phosphorus contained in the metaphosphate remains as calcium pyrophosphate:—

$$2Ca(PO_3)_2 + 5C = 2P + 5CO + \underset{\text{Calcium pyrophosphate.}}{Ca_2P_2O_7}.$$

The liberated phosphorus escapes in vapor form, and is collected and condensed under water in receivers of peculiar construction. To remove mechanically admixed impurities the phosphorus is again distilled from retorts and fused under water; it is then moulded into sticks.

The *crystalline* or *yellow* phosphorus obtained by distillation is a waxy, transparent, slightly yellow-colored substance, with specific gravity of 1.83 at 10° C. At ordinary temperatures it is soft and tough; at 0° it becomes brittle. It fuses under water at 44.4° and boils at 290° C. (278.3°). By the action of sunlight it becomes yellow, and is coated with a non-transparent, reddish-white layer. Phosphorus is insoluble in water, slightly soluble in alcohol and ether, and very readily soluble in carbon disulphide. It crystallizes from the latter solution in forms of the isometric (rhombic dodecahedra) system. When exposed to moist air, it oxidizes to phosphorous acid (H_3PO_3); the white vapors which arise contain ammonium nitrite (NH_4NO_2), ozone and hydrogen peroxide. Its odor resembles that of ozone. In the air it phosphoresces at night. It does this also in other gases, but only in such as contain oxygen. It appears the phosphorescence is influenced by the formation and combustion of the self-inflammable phosphine, as all substances which destroy the latter, prevent and put an end to the former. It is noteworthy that in pure oxygen the oxidation of phosphorus begins at 27°. If the oxygen be diluted by removal over an air pump or by the addition of neutral gases, so that its quantity is not more than 40 per cent., the absorption will be very energetic at 20°, but cease entirely at 7°.

Another modification—the *red or amorphous phosphorus*—possesses properties entirely different from the ordinary variety. It is a reddish-brown amorphous powder, of specific gravity 2.14; insoluble in carbon disulphide, non-phosphorescent, does not alter in the air, and is, indeed, very stable. While ordinary phosphorus is very poisonous, this variety is perfectly harmless. It does not fuse at a red heat, even when subjected to strong pressure, and vaporizes very slowly (above 260°), although only partially, the vapors passing over into ordinary phosphorus.

To prepare the red variety, yellow phosphorus is heated for some minutes to 300°, in closed, air-tight iron vessels; there is a partial conversion at 250°. The resulting mass is then treated with carbon disulphide or sodium hydroxide, to withdraw the unaltered, ordinary phosphorus. If some iodine be added to the ordinary phosphorus, the change will occur below 200°.

A third modification—*metallic phosphorus*—is formed if the amorphous variety be heated in a glass tube, free of air, to 530°. Microscopic needles then sublime into the upper, less heated, portion of the tube. It is more easily obtained if phosphorus is heated with lead, in a closed tube, to a red heat. The molten metal dissolves the phosphorus, and on cooling, the latter separates in black, metallic, shining crystals. Metallic phosphorus possesses the specific gravity 2.34, vaporizes with difficulty, and is less active than the amorphous variety.

Two green lines characterize the spectrum of phosphorus. On conducting hydrogen over a small piece of phosphorus, heated in a glass tube, the escaping gas will burn with a bright green flame. When ordinary phosphorus is distilled with water, some passes over with the steam and, in the dark, phosphoresces. This procedure serves for the detection of phosphorus in poisoning by this substance.

The density of P equals 62.06 ($H = 1$), or 4.29 ($air = 1$); the molecular weight is, therefore, 124.12. As the atomic weight of P is 31.03, it follows that the molecule in the form of vapor consists of 4 atoms: $P_4 = 124.12$ (31.03×4). We saw that the sulphur molecule at 500° consists of 6 atoms (S_6), and at 900° of 2 atoms (S_2). Such a dissociation does not, however, occur with phosphorus; even at 1040° its vapor density remains unaltered, although a partial dissociation does take place at a very intense heat.

When phosphorus is burned in oxygen or in air, it forms the pentoxide (P_2O_5). The ordinary variety inflames at 40°, and also by gentle friction; the amorphous is not ignited below 260°. The first will burn with a bright flame even under water. To this end heat some pieces of P in a flask with water, until they fuse, and conduct a current of oxygen through the water. Phosphorus combines very energetically with Cl, Br, and I at ordinary temperatures; by throwing a small piece of it into a vessel containing dry chlorine gas it at once inflames. The red only reacts with the halogens after applying heat. With most of the metals phosphorus unites on warming, and precipitates some of them from solutions of their salts. From a silver nitrate solution, it precipitates silver and phosphorus-argentide (PAg_3); this solution, therefore, answers as a counter-irritant in phosphorus burns.

The difference in deportment of the yellow and the amorphous phosphorus is fully accounted for by the circumstance, that when the amorphous is produced from the yellow there follows a considerable heat-disengagement:—

$$\text{P-yellow} = \text{P-amorphous} + 19.2 \text{ Cal.}$$

Hence, the red variety contains much less energy than the yellow. In its union with other substances there will always be liberated 19.2 Cal. less, and the reaction consequently will proceed more sluggishly and with less energy.

COMPOUNDS OF PHOSPHORUS WITH HYDROGEN.

PH_3, P_2H_4, P_4H_2.

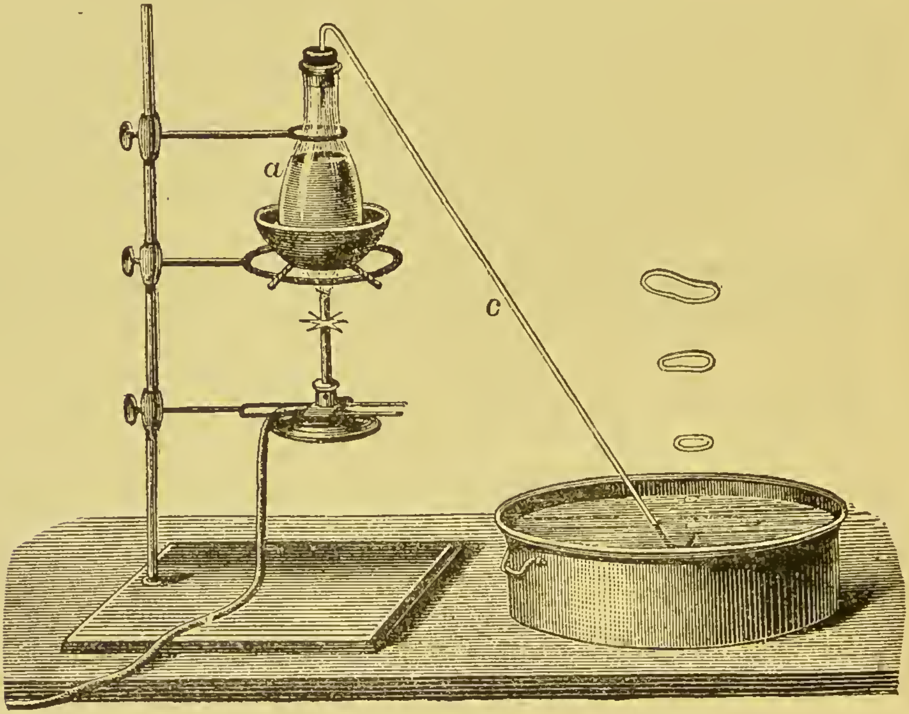
The compounds of phosphorus with hydrogen can be prepared by the action of nascent hydrogen upon phosphorus, as, for example, on gently heating dilute sulphuric acid with zinc and phosphorus (p. 145.) The usual course is to heat yellow phosphorus with concentrated potassium or sodium hydroxide, when spontaneously inflammable phosphine will escape and a salt of hypophosphorous acid enter solution.

The liberated gas mixed with air in a closed vessel explodes violently, hence to make it proceed as follows: Fill a glass flask almost full of aqueous KOH, add a few pieces of P, and heat over a lamp (Fig. 73). When the liberation of gas commences, and the air in the neck of the flask has been expelled, close the same with the cork of the delivery tube, the other end of which dips under *warm* water, to prevent any obstruction arising in it from phosphorus that may be carried over and solidify by cooling. Each bubble rising from the liquid inflames in the air, and forms white cloud-rings which ascend.

The gas thus produced consists of gaseous phosphine (PH_3) and hydrogen, with which is mixed a small quantity of a liquid substance (P_2H_4), whose presence imparts the spontaneous inflammability to the gas. On conducting the latter through a cooled tube the P_2H_4 is condensed to a liquid, and the escaping gas no longer inflames spontaneously. The liquid compound may be isolated in a similar manner if the gas is conducted through alcohol or ether, which will absorb the compound P_2H_4.

Liquid Phosphine, P_2H_4, separated from the gas by cooling, is a colorless, strongly refracting liquid, insoluble in water, and boiling at 30°. It inflames spontaneously in the air, and burns with great brilliancy to phosphorus pentoxide and water. Its presence in combustible gases, such as hydrogen, marsh gas, and PH_3, gives to them their spontaneous inflammability. In contact with some compounds, like carbon and sulphur, and by the action of sunlight, it decomposes into gaseous and solid phosphine:—

FIG. 73.



$$5P_2H_4 = 6PH_3 + P_4H_2.$$

Solid Phosphine, P_4H_2,(?) is a yellow powder, inflamed at 160° or by a blow. It is produced in the decomposition of calcium phosphate by hydrochloric acid.

Gaseous Phosphine, PH_3, may be formed, in addition to the manner previously described, by the action of water or hydrochloric acid upon calcium phosphide:—

$$Ca_3P_2 + 6HCl = 3CaCl_2 + 2PH_3.$$

Further, by the ignition of phosphorous and hypophosphorous acids:—

$$\underset{\text{Phosphorous acid.}}{4H_3PO_3} = PH_3 + \underset{\text{Phosphoric acid.}}{3H_3PO_4}.$$

It is a colorless gas, with a disagreeable, garlic-like odor, and is somewhat soluble in alcohol. Its density is 17.01 (H = 1), or 1.176 (air = 1). When pure—freed of P_2H_4—it ignites at 100° C. Oxidizing agents convert it again into the spontaneously inflammable variety, owing to the production of P_2H_4. It is extremely poisonous. Phosphine is decomposed into phosphorus and hydrogen when it is heated, or if it is exposed to the action of the electric spark. When ignited in the air it burns with a brightly luminous flame, disseminating at the same time a white cloud of phosphorus pentoxide (P_2O_5). Heat and the electric current decompose PH_3 into phosphorus and hydrogen. When mixed with chlorine it explodes violently, with production of phosphorus trichloride and hydrogen chloride:—

$$PH_3 + 3Cl_2 = PCl_3 + 3HCl.$$

Like ammonia, phosphine possesses faint alkaline properties, and combines with hydrogen iodide and bromide to yield compounds similar to ammonium chloride:—

$$PH_3 + HI = PH_4I.$$

It combines with HCl at —30° to —35°, or, at ordinary temperatures, under a pressure of 20 atmospheres. The group PH_4, figuring in the rôle of a metal in these compounds, is analogous to ammonium (p. 129), and termed *Phosphonium.*

Phosphonium Iodide, PH_4I. It is best prepared by the decomposition of phosphorus di-iodide (PI_2), by a slight quantity of water, or by adding yellow phosphorus (10 parts), and, after some hours, iodine (2 parts), to a saturated solution of hydriodic acid (22 parts). The liquid becomes a solid mass, consisting of phosphonium iodide and phosphorous acid. Phosphonium iodide sublimes in colorless, shining, cube-like rhombohedra; fumes in the air, and, with water, decomposes into PH_3 and HI. When decomposed by potassium hydroxide it yields pure hydrogen phosphide, which is not spontaneously inflammable:—

$$PH_4I + KOH = KI + PH_3 + H_2O.$$

Phosphine is a feebly exothermic compound:—

$$\text{P-yellow} + 3H = PH_3 + 11.6 \text{ Cal.}$$

This explains why in its power to react it differs so little from the elements composing it.

MOLECULAR FORMULA OF PHOSPHINE. ATOMIC WEIGHT OF PHOSPHORUS.

The analysis of phosphine shows that it consists of 1 part hydrogen and 10.34 parts phosphorus. Were its molecular formula PH, the atomic weight of P would be 10.34. The great analogy of phosphine to NH_3, and that of all the P compounds to those of N, argues, however, for the formula PH_3. The atomic weight of P, therefore is 31.03 ($= 3 \times 10.34$), and the molecular weight of the phosphine is 34.03 :—

$$\begin{array}{rl} H_3 &= 3 \\ P &= 31.03 \\ \hline PH_3 &= 34.03 \end{array}$$

This view is confirmed by the density which, according to its formula, must be $\frac{34.03}{2} = 17.01$. Direct experiment confirms this. Further, from the formula PH_3 it follows that 3 volumes of hydrogen are present in 2 volumes of the gas :—

$$\underset{\text{2 vols.}}{2PH_3} \text{ contain } \underset{\text{3 vols.}}{3H_2},$$

or in 1 volume there are 1½ volumes of hydrogen. On decomposing the gas in a eudiometer by means of electric sparks, it will be found that the volume increases 1½ times; the gas consists, then, of pure hydrogen, while phosphorus separates in a solid condition. As the phosphorus molecule in the gaseous condition is composed of 4 atoms, the phosphorus (62.06 parts) separated from 2 volumes of PH_3, will fill ½ volume when in the form of vapor; hence in 2 volumes of PH_3 there are present 3 volumes of H and ½ volume of phosphorus vapor.

Or, written molecularly :—

$$\underset{\text{1 vol.}}{P_4} + \underset{\text{6 vols.}}{6H_2} = \underset{\text{4 vols.}}{4PH_3}.$$

COMPOUNDS OF PHOSPHORUS WITH THE HALOGENS.

Phosphorus combines directly with the halogens to yield compounds of the forms PX_3 and PX_5, in which X indicates an halogen atom.

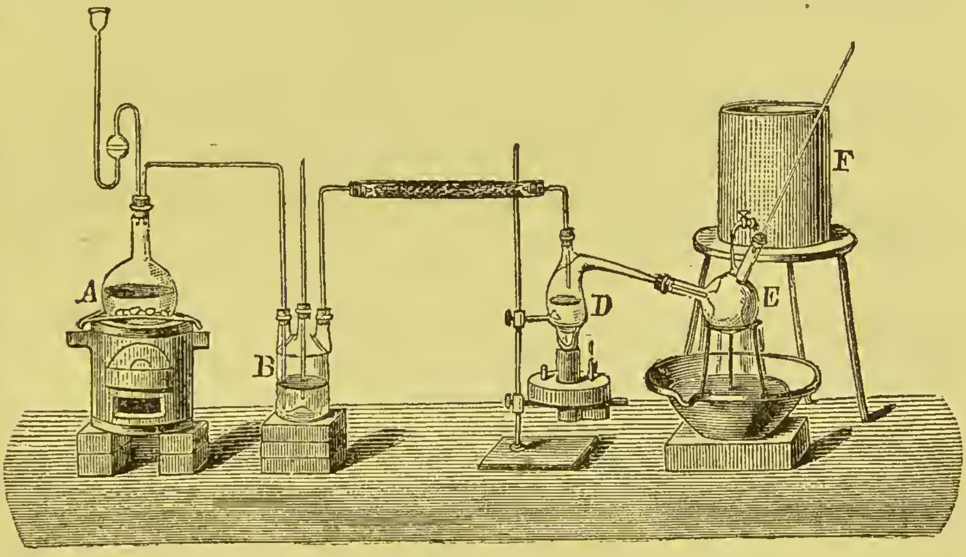
Phosphorus Trichloride—*Phosphorous Chloride*—PCl_3. Conduct dry chlorine gas over phosphorus gently heated in the retort *D* (Fig. 74). The phosphorus ignites in the stream of gas, and distils over as trichloride, which is collected in the receiver *E*, and condensed. The product is purified by a second distillation. It is a colorless liquid, boiling at 74° C., and has a sharp, peculiar odor. Its specific gravity equals 1.616 at 0°. It fumes strongly in the air, and is decomposed by moisture into phosphorous and hydrochloric acids:—

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

The vapor density of the trichloride equals 68.6 ($H = 1$), corresponding to the molecular formula $PCl_3 = 137.3$.

Phosphorus Pentachloride—*Phosphoric Chloride*—PCl_5.—This is produced by the action of an excess of chlorine upon the liquid trichloride. It is a solid, crystalline, yellowish-white compound. It fumes strongly in the air and sublimes without fusion when heated. It at the same time sustains a partial decomposition into trichloride and chlorine.

FIG. 74.



At lower temperatures (in an atmosphere of chlorine) the vapor density of the pentachloride has been found to be 104.1, corresponding to the molecular formula PCl_5 $(\frac{208.2}{2}) = 104.1$. At increased temperatures the vapor density steadily diminishes, and a gradual decomposition occurs—dissociation (p. 94) of the molecules PCl_5 into the molecules PCl_3 and Cl_2. The dissociation is complete at 236°, and then equals the vapor density 52; *i. e.*, the vapor then fills a volume twice as large as at a lower temperature. The breaking up of PCl_5 into PCl_3 and Cl_2 explains this:—

$$1 \text{ vol. } PCl_5 = 1 \text{ vol. } PCl_3 + 1 \text{ vol. } Cl_2.$$

That such a decomposition of the penta- into trichloride and chlorine does really occur, is proven, among other things, by the originally colorless vapor gradually assuming the yellow color of chlorine as the temperature rises. The decomposition products—PCl_3 and Cl_2—may be separated from each other by diffusion (p. 124).

PCl_5 acts very energetically with water, when it yields phosphoric acid (see this) and hydrochloric acid. With a little water it forms the oxychloride and hydrochloric acid:—

$$PCl_5 + H_2O = PCl_3O + 2HCl.$$

Phosphorus Oxychloride—$POCl_3$, is a colorless liquid, fuming strongly in the air, with a specific gravity, at 12°, of 1.7. It boils without decomposition at 110°. Its vapor density equals 76.7, corresponding to the molecular formula $POCl_3 = 153.4$. Water decomposes it into metaphosphoric and hydrochloric acids:—

$$POCl_3 + 2H_2O = HPO_3 + 3HCl.$$

This oxychloride may be obtained by decomposing the pentachloride with a little water (see above), or by letting it gradually deliquesce in moist air. The most practical method is the distillation of PCl_5, with an excess of phosphorus pentoxide:—

$$3PCl_5 + P_2O_5 = 5POCl_3,$$

or with crystallized boric acid (5 pts. with 1 pt.):—

$$3PCl_5 + 2BO_3H_3 = 3POCl_3 + B_2O_3 + 6HCl.$$

Its production on conducting ozonized air through phosphorous chloride is quite interesting:—

$$PCl_3 + O_3 = PCl_3O + O_2.$$

Potassium chlorate acts quite energetically upon phosphorous trichloride, with formation of the oxychloride (Dervin):—

$$3PCl_3 + ClO_3K = 3PCl_3O + KCl.$$

Phosphorus Sulpho-chloride, PCl_3S, is analogous to the preceding compound. It results from the union of the trichloride with sulphur when heated together to 130°, and also by the action of the pentachloride upon hydrogen sulphide or some metallic sulphides:—

$$PCl_5 + H_2S = PCl_3S + 2HCl.$$

It is a colorless liquid of sp. gr. 1.6 and boils at 124°. It fumes in the air and is decomposed by water according to the following equation:—

$$PCl_3S + 4H_2O = PO_4H_3 + 3HCl + H_2S.$$

The bromine and iodine phosphorus compounds are perfectly analogous to the chlorine derivatives. They are obtained by uniting the constituents in the proportions by weight expressed by their formulas. As the union is exceedingly energetic, it is best to proceed as follows: Dissolve the phosphorus in carbon disulphide, gradually add the calculated amount of Br or I, and then distil off the volatile solvent.

Phosphorus Tribromide, PBr_3, is a colorless liquid, boiling at 175°, and having a specific gravity of 2.7. The pentabromide, formed by the gradual addition of 2Br to PBr_3, is a yellow, crystalline substance, which fuses when heated, and breaks up into PBr_3 and Br_2. Water decomposes both compounds, as it does the corresponding chlorides. **Phosphorus oxy-bromide** ($POBr_3$) is a colorless crystalline mass, fusing at 45°, and boiling at 195°.

Phosphorus Chlor-bromide, PCl_3Br_2, is produced by the union of PCl_3 with Br_2 in the cold. It is a yellowish-red mass, which decomposes at 35° C., into PCl_3 and Br_2.

Phosphorus Tri-Iodide—PI_3, forms red crystals, fusing at 55° and distils, with partial decomposition, at a higher temperature. The so-called phosphorus iodide, PI_2, or P_2I_4 (corresponding to P_2H_4), crystallizes in beautiful orange-red needles or prisms, and fuses at 110°. Its vapor density at 265° and 90.7 mm. pressure equals 234, corresponding to the molecular weight P_2I_4. A little water decomposes it into phosphorous acid, PH_3 and HI. The last two bodies then form *phosphonium iodide*, PH_4I (p. 139).

The recently discovered **Phosphorus Pentafluoride**—PFl_5—is interesting. It results upon heating PCl_3 or PCl_5 with arsenic trifluoride, $AsFl_3$:—

$$3PCl_5 + 5AsFl_3 = 3PFl_5 + 5AsCl_3.$$

It is a colorless gas that fumes in moist air and is decomposed by water into phosphoric acid and hydrogen fluoride. Its density is 63, corresponding to the molecular formula $PFl_5 = 126.03$. It may be liquefied at 16° under a pressure of 46 atmospheres, and solidifies when the pressure is removed.

It is rather remarkable that although phosphorus pentaiodide could not be obtained, the stability of the compounds, PBr_5, PCl_5, PFl_5, gradually increases with the diminution of the atomic weight of the combined halogens. PFl_5 can be gasified without decomposition.

Thermo-chemical Deportment.—While the halogen derivatives of nitrogen (like those of oxygen) are strongly endothermic, are produced with the absorption of much heat, and are, in consequence, readily exploded (p. 134), those of phosphorus are exothermic. The heat disengaged in the union of yellow phosphorus and chlorine (p. 137) corresponds to the following symbols:—

$$(P,Cl_3) = 75.3; \ (P,Cl_5,) = 104.9; \ (P,Cl_3,O) = 142.6.$$

In this we observe a transition to the halogen derivatives of the metals, all of which are exothermic. In accordance with this (just as with the metals) we find that the heat of formation of the bromides and iodides diminishes in regular succession:—

$$(P,Br_3) = 42.6; \ (P,I_3) = 10.9.$$

The great reactivity of all these derivatives with water is fully explained by the large amount of heat set free at the same time.

3. ARSENIC.

$As = 75$. $As_4 = 300$. Vapor density, 150.

Arsenic is a perfect analogue of phosphorus, but possesses a somewhat metallic character. In its free state it is similar to metals.

Arsenic is found free in nature, although it occurs more frequently in combination with sulphur (realgar, orpiment), with oxygen (arsenolite, As_2O_3), and with metals (mispickel, FeSAs, cobaltite, CoAsS). To prepare it, heat mispickel with some iron, and free arsenic will sublime. Or, in the customary way of isolating metals from their oxides, heat the trioxide (arsenolite) with charcoal:—

$$As_2O_3 + 3C = 2As + 3CO.$$

Arsenic appears in two modifications. *Crystallized* arsenic is obtained by the sublimation of ordinary arsenic. It forms a gray-white, more or less metallic, crystalline mass, but may be changed into acute rhombic octahedra. Its specific gravity equals 5.7. It is brittle, and may be pulverized without difficulty.

The *amorphous* variety is formed when arsenic is sublimed in a glass tube in a current of hydrogen, and also upon heating arsine. It is black, with little lustre, and possesses the sp. gr. 4.71. When heated to 360° it sets heat free and reverts to the crystalline variety.

Away from air contact and at the ordinary pressure, arsenic vaporizes at a dark-red heat (about 450°) without previously fusing; it will, however, fuse if heated under great pressure in a sealed tube. Its vapor possesses a lemon-yellow color. The vapor density is 150 ($H = 1$), the molecular weight, therefore, 300. As its atomic weight equals 75, it follows that the molecule in the state of gas, like that of phosphorus, consists of four atoms ($As_4 = 300 = 4 \times 75$). It is only at a yellow heat that the vapor density alters any.

Arsenic does not change in dry air. When heated in the air it inflames at 180° and burns with a blue-colored flame, disseminating the garlic-like odor of arsenic tri-oxide (As_2O_3). It combines directly with most elements. Powdered arsenic will inflame when projected into chlorine gas. It yields arsenides with the metals.

It is remarkable that arsenic, belonging to the nitrogen group and generally forming compounds which in constitution are quite different from those of sulphur, should be analogous to the latter in its metallic combinations. Thus the sulphides and arsenides have similar formulas, are isomorphous, and in them sulphur and arsenic can mutually replace each other in atomic ratios, *e.g.*:—

$$FeS_2, FeAs_2 \text{ and } Fe(SAs).$$

COMPOUNDS OF ARSENIC WITH HYDROGEN.

Arsine, $AsH_3 = 78$. Like nitrogen and phosphorus, arsenic furnishes a gaseous compound containing 3 atoms of hydrogen. It is obtained pure by the action of dilute sulphuric acid or hydrochloric acid upon an alloy of zinc and arsenic:—

$$As_2Zn_3 + 6HCl = 3ZnCl_2 + 2AsH_3.$$

It also results in the action of nascent H (zinc and sulphuric acid), upon many arsenic compounds, as, *e. g.*, the tri-oxide:—

$$As_2O_3 + 6H_2 = 2AsH_3 + 3H_2O.$$

Arsine is a colorless gas, of strong, garlicky odor, and extremely poisonous action; it may be condensed to a liquid at —40°. Its density equals 38.9 ($H = 1$), or 2.69 ($air = 1$). It burns with a bluish-white flame when ignited, and evolves white fumes of arsenic tri-oxide:—

$$2AsH_3 + 3O_2 = As_2O_3 + 3H_2O.$$

It is decomposed at a dull red heat or by the electric spark into arsenic and hydrogen. On conducting the gas through a heated tube the arsenic deposits itself behind the heated part as a metallic coating (*arsenic mirror*). On holding a cold object, *e. g.*, a piece of porcelain in the flame of the gas, the arsenic forms a black deposit (arsenic spots). In its chemical behavior arsine is very similar to PH_3; its basic properties are very slight, and it does not furnish any derivatives with the halogens.

According to analysis, arsine consists of 1 part by weight of hydrogen and 25 parts arsenic. If, because of its analogy to PH_3, we ascribe to it the formula AsH_3, then the atomic weight of arsenic would be 75 (3×25) and the molecular weight of AsH_3 would = 78. Hence the density must be $\frac{78}{2} = 39$, which is confirmed by experiment. The formula, too, shows that 3 volumes of hydrogen are present in 2 volumes of AsH_3:—

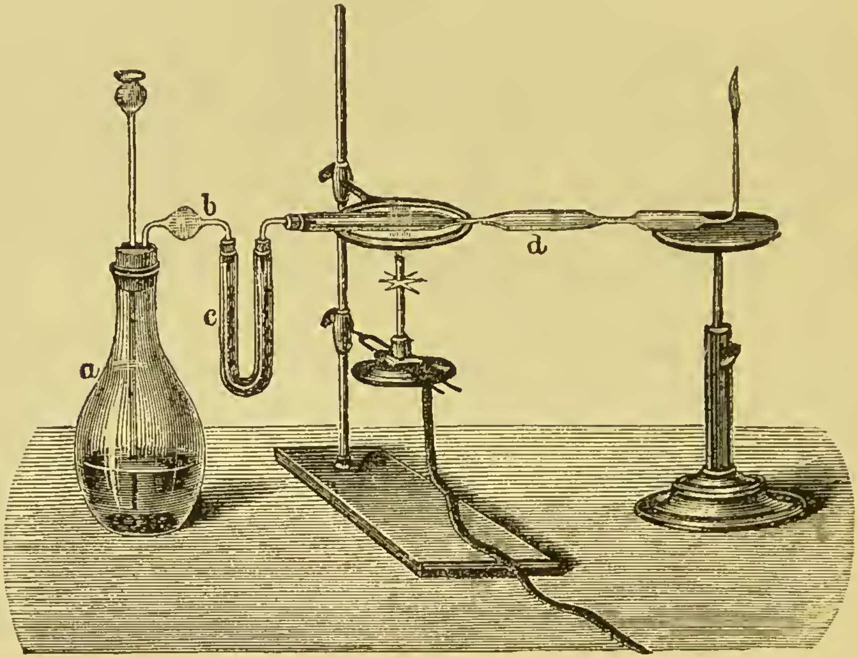
$$\underset{\text{2 vols.}}{2AsH_3} \text{ contain } \underset{\text{3 vols.}}{3H_2}.$$

We can satisfy ourselves of this by decomposing the gas by electricity in a eudiometer (see p. 140).

Marsh's Method for the Detection of Arsenic.—The detection of arsenic is very important, because of the poisonous nature of the element. The method of Marsh is based upon the formation and the characteristic properties of arsine. It is as follows: Hydrogen is generated in a flask *a* (Fig. 75), by the action of dilute sulphuric acid upon zinc, and a portion of the solution to be tested for arsenic is introduced through the funnel-tube. The liberated gas, a mixture of hydrogen and arsine, is dried in the calcium chloride tube *c* and escapes through the difficultly fusible glass tube *d*, which is contracted at several points. Upon igniting the escaping hydrogen (after all the air has been previously expelled from the vessel, as otherwise oxy-hydrogen gas will be present) it will burn with a bluish-white flame, if arsenic is present, and at the same time disseminate a white vapor. The dark arsenic spots are obtained by holding a cold porcelain dish in the flame. If the tube *d* be heated (as shown in Fig. 75), an arsenic mirror will be formed upon the adjacent contraction. The slightest traces of arsenic may be detected by this method.

Besides the ordinary arsine, AsH_3, we might expect the existence of As_2H_4 and As_4H_2, corresponding to the liquid and solid phosphines (P_2H_4 and P_4H_2). The first is not known; its derivatives exist, and contain hydrocarbon groups instead of hydrogen. An example of this class is cacodyl, $As_2(CH_3)_4 = (CH_3)_2$-As–$As(CH_3)_2$. Nitrogen affords similar compounds—$(CH_3)_2N–NH_2$ and $(CH_3)NH–NH_2$, derived from diamide or hydrazine ($N_2H_4 = H_2N–NH_2$).

FIG. 75.



The **solid arsine**, As_4H_2, is obtained by the action of nascent hydrogen upon arsenic compounds in the presence of nitric acid. It forms a reddish-brown powder, which decomposes when heated.

COMPOUNDS OF ARSENIC WITH THE HALOGENS.

These are perfectly analogous to the corresponding phosphorus compounds, and are the result of the direct union of their constituents. The iodide is the only known representative of the compounds with the formula AsX_5 (see p. 140). The metallic character of arsenic is shown by the fact that arsenic chloride, like other metallic chlorides, may be obtained by the action of hydrochloric acid upon the oxide:—

$$As_2O_3 + 6HCl = 2AsCl_3 + 3H_2O.$$

Arsenic chloride is evolved when a solution of As_2O_3 is boiled with concentrated hydrochloric acid.

Arsenic Trichloride—$AsCl_3$. A colorless, oily liquid, fuming in the air, and having a specific gravity of 2.2. It solidifies at —30° and boils at 134°. Its vapor density equals 90.5 ($H = 1$), corresponding to the molecular formula $AsCl_3 = 181.0$. The chloride dissolves in a small quantity of water without change, while much water converts it into the oxide and hydrochloric acid:—

$$2AsCl_3 + 3H_2O = As_2O_3 + 6HCl.$$

Arsenic Tribromide, $AsBr_3$, is a white crystalline mass, fusing at 20°, and boiling at 220° C. The **Tri-iodide**, AsI_3, forms red crystals; the **Trifluoride**, $AsFl_3$, is a liquid, fuming strongly in the air. It results in the distillation of $AsCl_3$ or As_2O_3 with calcium fluoride and sulphuric acid. **Arsenic pentaiodide**, AsI_5, melts at 70°, and is very soluble in water and alcohol.

Thermo-chemical Deportment.—The arsenic halogen derivatives are exothermic (see p. 143). Their heats of formation correspond to the symbols:—

$$(As,Cl_3) = 71.4; \quad (As,Br_3) = 47.1; \quad (As,I_3) = 12.6.$$

This readily explains their chemical behavior. The following thermo-chemical equation, based on the principle of the greatest heat disengagement (p. 67), indicates that arsenic trioxide is converted by gaseous or concentrated hydrochloric acid (see above) into arsenic trichloride:—

$$\underset{154.6}{As_2O_3\text{-solid}} + \underset{6 \times 22.0}{6HCl\text{-gas}} = \underset{2 \times 71.4}{2AsCl_3} + \underset{3 \times 68.3}{3H_2O} \; . \; . \; . \; (+ 61.1 \text{ Cal.})$$

If, however, dilute hydrochloric acid be used the thermal value on the right side is negative:—

$$\underset{147}{As_2O_3 \text{ dissolved}} + \underset{6 \times 39.3}{6HCl \text{ in solution}} = \underset{2 \times 71.4}{2AsCl_3} + \underset{3 \times 68.3}{3H_2O} \; . \; . \; . \; (-35.1 \text{ Cal.})$$

The reaction consequently pursues an inverse direction. Dilute hydrochloric acid cannot convert the trioxide into the trichloride, but the latter, on the other hand, is fully changed into the former and hydrochloric acid by much water. The course of the reaction manifestly is dependent upon the concentration of the solution and is influenced by the heat of solution (pp. 68 and 93).

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4. ANTIMONY.

$Sb = 120.3.$

The metallic character exhibited by arsenic becomes more distinct with antimony, which at the same time retains its complete analogy to the metalloidal elements, arsenic and phosphorus. Antimony is a perfect metal so far as its physical properties are concerned.

It (Stibium) occurs in nature chiefly in union with sulphur, as stibnite, Sb_2S_3, and with sulphur and metals in many ores. It is almost always accompanied by arsenic. To prepare antimony, stibnite is roasted in a furnace, *i. e.*, heated with air access, whereby the sulphur burns, and antimony trioxide remains :—

$$Sb_2S_3 + 9O = Sb_2O_3 + 3SO_2.$$

The residual oxide is ignited with carbon, which reduces it to metal (general procedure for the separation of metals). Antimony may also be obtained by heating its sulphide with iron, which combines with the sulphur :—

$$Sb_2S_3 + 3Fe = 2Sb + 3FeS.$$

The resulting commercial crude antimony is further purified in the laboratory by fusing it with nitre, whereby the admixed arsenic, sulphur and lead are removed. Chemically pure antimony is obtained by reducing the pure oxide.

It is a silver-white, and very brilliant metal, of leafy crystalline structure ; specific gravity 6.715. Like arsenic it crystallizes in rhombohedra, is very brittle, and may be easily broken. It fuses at 430°, and distils at a white heat. It is not altered in the air at ordinary temperatures; but when heated it burns with a blue flame, yielding white vapors of antimonic oxide, Sb_2O_3. Like phosphorus and arsenic it combines directly with the halogens ; powdered antimony inflames in chlorine gas. It is insoluble in hydrochloric acid ; nitric acid oxidizes it to antimonic oxide.

Hydrogen Antimonide—*Stibine*—(SbH_3), is produced like arsine, and is very similar to the latter. It is always obtained mixed with hydrogen. It is a colorless gas of peculiar odor, and when ignited, burns with a greenish-white flame, disseminating white vapors of antimonic oxide. A red heat decomposes it into antimony and hydrogen. In Marsh's apparatus (Fig. 75, p. 146) it affords an antimony mirror and spots. The mirror is distinguished from that of arsenic by its black color, lack of lustre, its insolubility in a solution of sodium hypochlorite (NaClO), and by its slight volatility in a current of hydrogen.

When a solution of antimony trichloride is decomposed by the electric current there is deposited on the cathode a metallic compound, which explodes when crushed, scratched with a knife, heated or exposed to the electric spark. White clouds of antimony chloride escape and pure metallic antimony remains. This explosive body was supposed to be an alloy of antimony with hydrogen. It, however, consists of metallic antimony, 4.8 to 8 per cent. of antimonious chloride, and some hydrogen chloride mechanically or chemically combined. The cause of the explosibility is unknown.

COMPOUNDS OF ANTIMONY WITH THE HALOGENS.

Antimonous Chloride—*Trichloride*—$SbCl_3$, results from the action of chlorine upon the metal or its sulphide; better by the solution of the oxide or sulphide in strong hydrochloric acid:—

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

This solution is evaporated to dryness and the residue distilled.

It is a colorless, crystalline, soft mass (*Butyrum Antimonii*), fusing at 73° and boiling at 223°. Its vapor density equals 112.8 ($H = 1$), corresponding to the molecular formula, $SbCl_3 = 225.7$. In the air it attracts water and deliquesces. It dissolves unchanged in water acidified with hydrochloric acid. Much water decomposes it; the solution becomes turbid and a white powder—powder of algaroth—separates:—

$$SbCl_3 + H_2O = SbOCl + 2HCl.$$

The composition of this powder varies with the conditions under which it is formed, but generally corresponds to the formula $2(SbOCl).Sb_2O_3$. Pure **Antimony Oxychloride**, $SbOCl$, obtained by heating $SbCl_3$ with alcohol, occurs in colorless crystals and is further decomposed by water.

While the metallic chlorides are not decomposed by water at ordinary temperatures, the ready decomposition of the halogen derivatives of antimony, shows that this element yet possesses a partial metalloidal character.

Antimonic Chloride—*Pentachloride*—$SbCl_5$, results from the action of an excess of chlorine upon antimony or the trichloride. It is a yellowish liquid which fumes in the air, becomes crystalline when cold and fuses at —6°. Heat partially decomposes it, like PCl_5, into $SbCl_3$ and Cl_2:—

$$\underset{\text{1 vol.}}{SbCl_5} = \underset{\text{1 vol.}}{SbCl_3} + \underset{\text{1 vol.}}{Cl_2}.$$

Water converts it into pyroantimonic acid ($H_4Sb_2O_7$), and hydrochloric acid.

Antimony Tribromide—$SbBr_3$—is a white, crystalline substance, fusing at 94° and distilling at 270°. The **Tri-iodide**, SbI_3, is a red compound, *crystallizing* in three distinct forms. The **Pentaiodide**, SbI_5, is dark brown in color and fuses about 78°.

The heat of formation of antimony chloride equals:—

$$(Sb,Cl_3) = 91.4.$$

We possess no knowledge concerning the other halogen derivatives in this direction. The decomposition of $SbCl_3$ by water is analogous to that of arsenic trichloride (p. 147).

We must also include **Bismuth**—Bi = 208—in the group of nitrogen, phosphorus, arsenic, and antimony; it forms similarly constituted compounds, *e. g.*, $BiCl_3$, BiI_3, $BiOCl$. Its metallic character, however, considerably exceeds its metalloidal. Thus, it does not unite with hydrogen, and the oxide (Bi_2O_3), similar in constitution to the acid-forming As_2O_3, possesses only basic characters. We will, therefore, consider bismuth and its derivatives with the metals.

TABULATION OF THE ELEMENTS OF THE NITROGEN GROUP.

The elements belonging here—nitrogen, phosphorus, arsenic, antimony, and bismuth—present similar graded differences in their physical and chemical properties, just like the elements of the chlorine and oxygen group, and this gradation is intimately connected with the atomic weights. As the latter increase the substance condenses, the fusibility and volatility decrease, and the metallic character becomes more prominent:—

	N.	P.	As.	Sb.
Atomic weight............	14.041	31.03	75	120.3
Specific gravity............	...	1.8–2.1	4.7–5.7	67
Fusion point................	...	44°	red-white heat	...
Vapor density.............	0.972	4.32	10.3	...

Excepting bismuth, which is perfectly metallic in its nature, the elements of this group form gaseous compounds with three atoms of hydrogen.

Ammonia (NH_3) possesses strongly basic properties, and combines with all acids to yield ammonium salts; phosphine (PH_3) combines with HBr and HI to form salt-like compounds. AsH_3 and SbH_3 no longer show basic properties. Arsenic and antimony, as well as the two preceding elements, combine with the hydrocarbons (*e. g.*, CH_3 and C_2H_5) and form compounds that are analogous in constitution and similar in character to the hydrides. These compounds [$As(CH_3)_3$ and $Sb(CH_3)_3$] will be described in Organic Chemistry; they possess basic properties and yield salts corresponding to the ammonium salts.

The oxygen derivatives of these elements exhibit a similar gradation. With increase of atomic weight, corresponding to the addition of metallic character, the oxides that form strong acids in the lower series acquire a more basic nature.

The gradation is more manifest in the thermal relations of the group. However, of the hydrides of the elements of this group only those of nitrogen and phosphorus have been investigated in this direction (pp. 129 and 137):—

$$(N,H_3) = 11.9; \quad (P,H_3) = 11.6.$$

It is very probable that in the case of the higher members (just as in the halogen and oxygen groups) the heat of formation will diminish successively in accordance with their increasing decomposability. Yet, the heat of formation of the halogen derivatives increases successively with rise of atomic weight and metallic character:—

$$(N,Cl_3) = -38.1; \ (P,Cl_3) = 75.3; \ (As, Cl_3) = 71.4; \ (Sb,Cl_3) = 91.4.$$

We here observe plainly the transition from metalloidal to metallic character.

CARBON GROUP.

The two non-metals, carbon and silicon, and the metals, tin and germanium, belong to this group. These unite with four atoms of hydrogen or four of the halogens.

1. CARBON.

$C = 12.$

Carbon occurs free in nature as the diamond and graphite. It constitutes the most important ingredient of all the so-called organic substances originating from the animal and vegetable kingdoms, and is especially contained in the fossilized products arising from the slow decomposition of vegetable matter—in turf, in brown coal, bituminous coal, and in anthracite. In combination with hydrogen it forms the so-called mineral oils—petroleum and asphaltum. It occurs, further, as carbon dioxide (CO_2) in the air; and in the form of carbonates (marble, calcite, dolomite) comprises many minerals and entire rock formations.

It is found in different allotropic modifications when free; these may be referred to the three principal varieties—diamond, graphite and amorphous carbon. In all these forms it is a solid, even at the highest temperatures; non-fusible and non-volatile. This deportment can only be explained by the supposition that its free molecules are composed of a large number of carbon atoms combined with each other. (See p. 107.) All the modifications of carbon are quite stable, but not very reactive. When burned all yield carbon dioxide.

1. The *diamond* occurs in alluvial soils in certain districts (in India, Brazil, and South Africa); less frequently in micaceous schist. It has great lustre, strong

power of refraction, and the greatest hardness of all substances. It crystallizes in forms of the regular system, that are mostly rhombic dodecahedra, rarely octahedra. Ordinarily, it is perfectly colorless and transparent; sometimes, however, it is colored by impurities. Its specific gravity equals 3.5. It does not soften any unless exposed to the most intense heat—between the poles of a powerful galvanic battery. It is then converted into a graphitic mass. When heated in oxygen gas it burns to carbon dioxide. It is scarcely attacked at all when acted upon by a mixture of nitric acid and potassium chlorate.

2. *Graphite* is characterized by its oxidation to graphitic acid when it is heated with a mixture of potassium chlorate and nitric acid. Like amorphous carbon, it is oxidized to mellitic acid by an alkaline solution of potassium permanganate, or when it is made the positive electrode in the electrolysis of alkaline solutions. Native graphite is found in the oldest rock formations, and of especially good quality at Altai, in Siberia. It occurs, too, in considerable quantities at many places in the United States. It is occasionally found crystallized in six-sided forms, but usually as an amorphous, grayish-black, glistening, soft mass, used in the manufacture of lead pencils. The specific gravity is 2.25. It conducts heat and electricity well. When away from air-contact it is not altered even at the highest temperatures. It usually burns when heated in an atmosphere of oxygen, but with more difficulty than the diamond, forming carbon dioxide, and leaving about 2–5 per cent. of ash. To purify the poorer and more impure kinds of graphite, the latter is pulverized and heated with a mixture of $KClO_3$ and H_2SO_4; the product is washed with water, and the residue ignited (Brody's Graphite).

Graphite may be obtained artificially by fusing amorphous carbon with iron; when the latter cools, a portion of the dissolved carbon separates in hexagonal shining leaflets.

3. *Amorphous Carbon* is produced by the carbonization of organic (containing carbon) substances, and is found in a fossilized state. Nitric acid and potassium chlorate convert it in the cold into brown substances soluble in water. The purest amorphous carbon is soot which is obtained by the imperfect combustion of resins and oils (like turpentine) rich in carbon. *Gas Carbon*, called metallic carbon, deposits in the manufacture of gas in the retorts, and is very hard, possessing metallic lustre, and conducting electricity well; hence its use in galvanic batteries. *Coke*, resulting from the ignition of bituminous coal, forms a sintered mass, conducting heat and electricity well. *Charcoal* is very porous, and can absorb many gases and vapors; 1 volume of it condenses 90 volumes NH_3, 55 volumes H_2S, and 9 volumes O_2. At 100°, and under the air pump, the absorbed gases are again liberated. Charcoal will also take up many odorous substances and decaying matter; hence is employed as a disinfectant. *Animal Charcoal* is obtained by the carbonization of animal matter (bones, blood, etc.), and possesses the power of removing many coloring substances from their solutions; hence it serves in the laboratory and in commerce for the decolorization of dark solutions.

All these varieties of carbon contain smaller or larger quantities of nitrogen, hydrogen, and mineral substances, which remain as ash after combustion. Hydrochloric acid will withdraw almost all the mineral constituents.

The fossil coal varieties, bituminous coal, lignite and turf, are the products of a peculiar, slow decay of wood fibre, which gradually separates oxygen and hydrogen, and enriches itself in carbon. Fossil coal contains 90 per cent. and brown coal 70 per cent. of carbon. The fossil coal richest in carbon, the last product of the alteration, is *anthracite*. This has lost all its organic structure, and contains 96–98 per cent. of carbon.

COMPOUNDS OF CARBON WITH HYDROGEN.

With hydrogen, carbon forms an unlimited number of compounds, into which all other elements, especially oxygen and nitrogen, can enter. The derivatives of carbon have been termed *organic compounds*, because they were formerly obtained exclusively from vegetable and animal organisms, and the idea was entertained that they were produced by the influence of forces other than those forming the mineral substances. At present, most carbon derivatives are prepared artificially from the elements by simple synthetic methods; we are aware that they do not differ essentially from mineral substances. Hence the description of the carbon compounds must be arranged in the general system of chemical bodies. This, however, is not readily executed without sacrificing the review of a defunct system. The derivatives of carbon are so numerous, and possess so many peculiarities, that it appears necessary, from a practical standpoint, to treat them apart from the other compounds, in a separate portion of chemistry, which we, pursuing the old custom, term organic chemistry. We then designate the chemistry of *all other bodies* as *Inorganic Chemistry.* Only the simplest carbon compounds will be considered here.

It is only under the influence of the electric arc that the direct union of carbon and hydrogen may be effected; the product is acetylene (C_2H_2). All other hydrocarbons are obtained indirectly in various ways.

Methane—*Marsh Gas*—CH_4.—This simplest hydrocarbon, containing but one atom of carbon, is formed in the decay of organic matter under water (in swamps and coal mines), and escapes in large quantities in many regions of the earth (thus at Baku, on the Caspian Sea). It may be obtained synthetically by conducting vapors of carbon disulphide and hydrogen sulphide over ignited copper filings:—

$$CS_2 + 2H_2S + 8Cu = 4Cu_2S + CH_4.$$

For its preparation, heat a mixture of sodium acetate with sodium hydroxide:—

$$C_2H_3NaO_2 + NaOH = CH_4 + Na_2CO_3.$$

Methane is a colorless, odorless gas, insoluble in water; it can be condensed by pressure and cold. Its density equals 8 ($H = 1$) or 0.552 ($air = 1$), corresponding to the molecular formula $CH_4 = 16$. Methane, under great pressure and at low temperatures (below — 82°), is condensed to a colorless liquid, which boils at — 164° under the ordinary pressure. Its specific gravity is 0.415 at the boiling point. When ignited it burns with a faintly luminous flame. It affords a violently explosive mixture (fire-damp of the miners) with two volumes of oxygen (or ten volumes of air):—

$$\underset{\text{1 vol.}}{CH_4} + \underset{\text{2 vols.}}{2O_2} = \underset{\text{1 vol.}}{CO_2} + \underset{\text{2 vols.}}{2H_2O}.$$

MOLECULAR FORMULA OF METHANE. ATOMIC WEIGHT OF CARBON.

The quantitative analysis of methane shows that for every 1 part of hydrogen in it there are 3 parts carbon. Were the formula CH (analogous to hydrochloric acid) then the atomic weight of carbon would be 3. If it corresponded to the formula of water (H_2O) then carbon would equal 6, etc. (see p. 98):—

$$\begin{array}{rcl} H & = & 1 \\ C & = & 3 \\ \hline CH & = & 4 \end{array} \qquad \begin{array}{rcl} 2H & = & 2 \\ C & = & 6 \\ \hline CH_2 & = & 8 \end{array} \qquad \begin{array}{rcl} 3H & = & 3 \\ C & = & 9 \\ \hline CH_3 & = & 12 \end{array} \qquad \begin{array}{rcl} 4H & = & 4 \\ C & = & 12 \\ \hline CH_4 & = & 16 \end{array}$$

In this case the analysis yields (as in former instances) no conclusive answer. We derive the molecular weight of methane, according to Avogadro's law, from its density. The latter equals 8 ($H = 1$), hence the molecular weight is 16. In 16 parts by weight of methane there are 4 parts by weight, hence 4 atoms, of hydrogen, and 12 parts carbon. The atomic weight of C is, then, presuming that only 1 atom of it is present in methane, 12:—

$$\begin{array}{lrcr} \text{4 atoms hydrogen} & H_4 & = & 4 \\ \text{1 atom carbon} & C & = & 12 \\ \hline \text{Methane molecule} & CH_4 & = & 16 \end{array}$$

That the atomic weight of carbon is really 12, is proven by the fact that of all its innumerable derivatives, not one contains less than 12 parts, by weight, of this element. It follows, with certainty, from the periodic system of elements (p. 80).

From the formula CH_4 it follows that in 1 volume of methane there are 2 volumes of hydrogen ($\underset{\text{1 vol.}}{CH_4}$ contains $\underset{\text{2 vols.}}{2H_2}$). This is proved indirectly by the combustion of methane with oxygen in a eudiometer (see p. 121). Four atoms of hydrogen yield two molecules of H_2O; 1 atom of C yields 1 molecule of CO_2. Hence the volume relation in the combustion of CH_4 in oxygen is expressed by the equation:—

$$\underset{\text{1 vol.}}{CH_4} + \underset{\text{2 vols.}}{2O_2} = \underset{\text{1 vol.}}{CO_2} + \underset{\text{2 vols.}}{2H_2O}.$$

In two volumes of aqueous vapor there are 2 volumes of hydrogen; hence in one volume of CH_4, there are 2 volumes of H_2. The result of the eudiometric analysis confirms these conclusions.

Ethane—C_2H_6—is formed when hydrogen *in statu nascendi* acts upon ethyl chloride:—

$$C_2H_5Cl + 2H = C_2H_6 + HCl.$$

Or by the action of potassium or sodium upon methyl iodide:—

$$2CH_3I + Na_2 = C_2H_6 + 2NaI.$$

This is a colorless gas, insoluble in water, and when ignited it burns with a feebly luminous flame. Its density equals 15 ($H = 1$) or 1.037 ($air = 1$) corresponding to the molecular formula $C_2H_6 = 30$.

Besides methane (CH_4) and ethane (C_2H_6) there exists a long series of hydrocarbons of the general formula C_nH_{2n+2} (*e. g.*, C_3H_8, C_4H_{10}, C_5H_{12}, etc.), in which each member differs from the preceding and next following by 1 C and 2 H (CH_2). Bodies belonging to such a series, greatly alike in their chemical behavior, are termed *homologues*. In addition to this series of *saturated* hydrocarbons others exist, with less hydrogen, and by the addition of the latter, pass into the *saturated*, and may, therefore, be termed *unsaturated*. The first *unsaturated* series is composed according to the formula C_nH_{2n}, the second according to C_nH_{2n-2}, etc. The lowest member of the series C_nH_{2n} is ethylene (see Chemical Structure, p. 170).

Ethylene—C_2H_4—is formed in the destructive distillation of wood, bituminous coal, and many carbon compounds, hence is contained in illuminating gas. It is most easily obtained by the action of sulphuric acid upon alcohol, whereby the acid withdraws H_2O from the latter:—

$$\underset{\text{Alcohol.}}{C_2H_6O} - H_2O = \underset{\text{Ethylene.}}{C_2H_4}.$$

It is a colorless gas, of weak, ethereal odor, and condenses at —110° to a liquid. Its density equals 14 ($H = 1$) or 0.969 ($air = 1$), corresponding to the molecular formula $C_2H_4 = 28$. Its critical temperature lies at + 9.2°, and its critical pressure is 58 atmospheres. Under a pressure of 1 atmosphere, liquid ethylene boils at —102°, and when in a vacuum at —150°. Because it does not solidify at this point, it is well adapted for the liquefaction of other gases (p. 48). It burns with a bright, luminous flame, decomposing first into marsh gas and free carbon:—

$$C_2H_4 = CH_4 + C.$$

The CH_4 then burns and heats the particles of carbon in the flame to incandescence; these are then consumed to carbon dioxide (CO_2).

The unsaturated compound, ethylene, unites directly with two atoms of chlorine and bromine:—

$$C_2H_4 + Cl_2 = C_2H_4Cl_2.$$

The resulting compounds, $C_2H_4Cl_2$ and $C_2H_4Br_2$, are oily liquids; hence the name olefiant gas, for ethylene.

The lowest member of the second unsaturated series is C_2H_2.

Acetylene—C_2H_2—is produced in the dry distillation of many carbon compounds, and is present in coal gas, to which it imparts a peculiar penetrating odor. Its density $= 13$ ($H = 1$) corresponding to the formula $C_2H_2 = 26$. It combines directly with 2 and 4 atoms of chlorine and bromine.

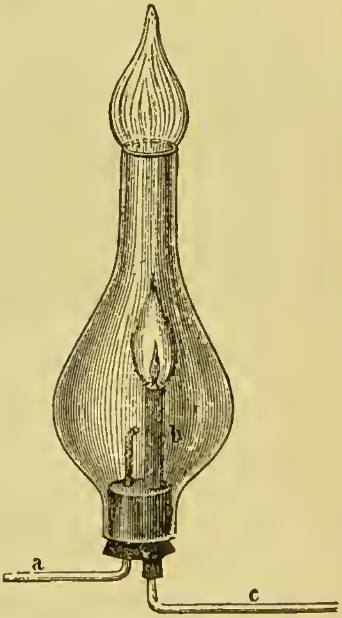
The three hydrocarbons considered above, methane (CH_4), ethylene (C_2H_4), and in slight amount acetylene (C_2H_2), constitute, together with H and carbonous oxide (CO), ordinary illuminating gas, which is produced in the dry distillation of bituminous coal, lignite, or wood. The illuminating power is influenced by its quantity of ethylene and acetylene (and their homologues.)

THE NATURE OF FLAME.

We are aware that every chemical union which occurs in a gaseous medium, and is accompanied by the evolution of light is designated combustion. We observe herein, that some bodies, like sulphur and phosphorus, yield a flame when burned in the air or in other gas; such substances are converted into gases or vapors at the temperature of combustion. Carbon burns without a flame, becomes incandescent, because it is non-volatile. The carbon compounds, wood, bituminous coal, and tallow, are, indeed, not volatile, but burn with a flame because under the influence of heat they develop combustible gases. Flame is, therefore, nothing more than a combustible gas heated to incandescence. We have observed, too, that the combustibility is only a relative phenomenon; if hydrogen burns in oxygen and chlorine, oxygen and chlorine, conversely, will burn in hydrogen (p. 57). Illuminating gas burns in the air, therefore air (its oxygen) burns in the former. This may be demonstrated in the same manner as in the case of chlorine and hydrogen.

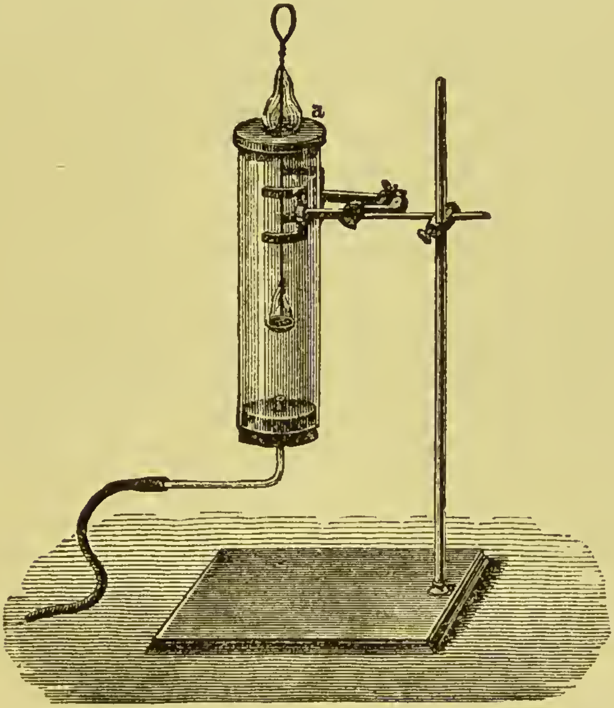
The relative combustibility and the so-called return of the flame may be very plainly illustrated by means of the following contrivance: An ordinary lamp chimney (Fig. 76) is closed at its lower end with a cork, through which two tubes enter; the narrow tube, *a*, somewhat contracted at its end, is connected with a gas stop-cock; the other tube, *b* (best a cork borer), is about 5 mm. wide, and communicates with the air. The gas issuing from the tube *a* is ignited, and the chimney is then dropped over the not too large flame; it continues to burn along quietly, as sufficient air enters through

Fig. 76.



the wide tube *b*. Upon increasing the supply of gas, the flame becomes larger, the globe fills with illuminating gas, while the air is crowded out. The gas flame is extinguished, and an air-flame appears upon the wider tube, *b*, as the entering air continues to burn, in the atmosphere of illuminating gas. The excess of the latter escaping from the upper portion of the globe may be ignited, and we then have a gas-flame above, while within the globe we have an air-flame. On again lessening the gas-flow the air-flame will distribute itself, extend to the exit of the tube *a*, and then the gas-flame will appear upon the latter, while the flame above the globe is extinguished. In this manner, we may repeat the return process of flames at will. That the air actually burns in the air-flame may be plainly proved if we introduce a small gas-flame from *c*, through the wide metallic tube *b*; the little flame will continue to burn in the air-flame, but will be extinguished if it be introduced higher up into the atmosphere of illuminating gas.

FIG. 77.



We say ordinarily that only those bodies are combustible which, because of their power to unite with oxygen, burn in an atmosphere of this gas or in air. If we imagine, however, an atmosphere of hydrogen, or illuminating gas, then bodies rich in oxygen must be combustible in these. In fact, nitrates, chlorates, etc., burn in an atmosphere of illuminating gas with the production of an oxygen flame. This may be demonstrated as follows: An Argand-lamp chimney (Fig. 77) is closed at its lower end by a cork, bearing a gas-conducting tube. The gas which escapes through the opening of the sheet covering, *a*, is ignited. Then the substance (potassium or barium chlorate, etc.) is introduced into the flame on an iron spoon provided with a long handle, heated to the temperature of decomposition (disengagement of oxygen), and the spoon then plunged through the opening into the gas atmosphere. The substance burns with a brilliant light, as the resulting oxygen flame is brightly colored by the vaporizing and reduced metallic salts.

The brilliancy or luminosity of a flame is influenced by the nature of the substances contained in it, also by its temperature and density. Incandescent gases shine very faintly *per se;* this is especially true when they are diluted. Thus hydrogen, ammonia and methane burn with a pale flame. Even sulphur burns in the air with a slightly luminous flame. If, on the contrary, sulphur or phosphine be permitted to burn in oxygen, or arsenic and antimony in chlorine gas, an intense display of light follows. This depends on the fact that the flame is not diluted by the nitrogen of the air, is therefore more condensed, develops a higher temperature, and the combustion products (SO_2, P_2O_5, PCl_3) or the evaporating substances are not immediately gasified. That the density of the flame of gases exercises a great influence upon the luminosity is proved by the fact that hydrogen, compressed into a smaller space with oxygen, burns with intense light display.

A slightly luminous flame may be rendered intense by introducing solid particles into it. For example, if hydrogen be passed through liquid chromium oxychloride (CrO_2Cl_2) it burns with a bright, luminous flame, because the volatile CrO_2Cl_2 in it is changed by the oxygen of the flame into solid, non-volatile chromium oxide, Cr_2O_3, whose particles are heated to incandescence by the hydrogen flame. The illuminating power of the various hydrocarbons and carbon compounds is similarly explained. Marsh gas, CH_4, and ethane, C_2H_6, afford a pale flame, because they burn directly to aqueous vapor and carbon dioxide. Ethylene, on the contrary, burns with a bright, luminous flame, because, by the temperature of combustion, it decomposes first into CH_4, and carbon, whose particles glow in the flame. (See p. 155.)

FIG. 78.

Let us consider the flame of an ordinary stearin candle: On approaching the wick with a flame the stearin melts, is drawn up by the fibres and converted into gaseous hydrocarbons, which ignite, and by their chemical union with the oxygen of the air, produce the flame. The unaltered gases exist in the inner non-volatile zone *a* (Fig. 78); they cannot burn because of lack of air access. If the lower end of a thin glass tube be inserted here the gases will rise in it, and may be ignited at the upper end. There is a partial combustion of the gases in the middle, luminous part, *f*, *e*, *g*; ethylene, C_2H_4, breaks up into CH_4 and C: the first burns completely, while the C is heated to a white heat, because there is not sufficient oxygen present for its combustion. The presence of carbon particles in the luminous part may be easily proved by placing a glass rod or a wire net in it; it will at once be coated with soot.

In the outer, very feebly luminous and almost invisible mantle, *b*, *c*, *d*, of the flame, which is completely surrounded by air, occurs the perfect combustion of all the carbon to carbon dioxide.

A perfectly identical structure is possessed by the ordinary illuminating gas flame. By bringing as much air or oxygen into it as is necessary for the perfect combustion of all the carbon, none of the latter separates (see below), and there is produced a faintly luminous but very hot flame. Upon this principle is based the construction of the Bunsen burner, the flame of which is employed in laboratories for heating and ignition. Fig. 79 represents a form of the same. The upper end, *c*, is screwed into the lower portion, and in the figure is only separated for the sake of explanation. The gas enters through the narrow opening, *a*, from the side gas tube, and mingles with air in the tube *c*, which enters through the openings of the ring, *b*. In this way we obtain a flame that is but faintly luminous, although affording an intense heat. On closing the openings in *b* the air is cut off, and the gas burns at the upper end of the tube *e*, with a bright, strongly smoking flame. The non-luminous flame contains an excess of oxygen, and hence oxidizes—*oxidizing flame*. It is employed to effect oxidation reactions. The luminous flame, on the other hand, is reducing in its action, and is designated the *reduction flame*, because the glowing carbon in it abstracts oxygen from many substances.

The construction and application of the ordinary and the gas blowpipes depend upon the same occurrences; they are, however, replaced at present by gas lamps.

The non-luminosity of the Bunsen burner flame, due to addition of air, depends on a more complete combustion of the separated carbon or of the yet undecomposed hydrocarbons. The flame, in consequence, is smaller, more intense, and the combustion extends itself even to the inner cone of the flame. It is more difficult to render the flame non-luminous by pure oxygen, because it is then not diluted by nitrogen, and is, therefore, much smaller, the temperature much higher, and the flame gases are more condensed.

Another variety of non-luminosity of hydrocarbon flames is induced by the admixture of inactive gases, like nitrogen and carbon dioxide. By this means the flame is enlarged and the combustion, as in the luminous flame, takes place only in the outer cone. In consequence of the dilution there are present fewer combustible particles in an equal space, and these can be more completely consumed by the oxygen of the air, which enters more readily; further, the temperature is lowered, and probably does not acquire the decomposition temperature of ethylene (C_2H_4) in the adjoining cone, which is being continually renewed. The simple extension of an illuminating flame upon a plate, will render it non-luminous, because then the air comes in contact with a larger flame surface. On heating a gas made non-luminous by the admixture of nitrogen, and then letting it burn, its flame becomes luminous because the increased temperature can induce the decomposition of ethylene.

Fig. 79.

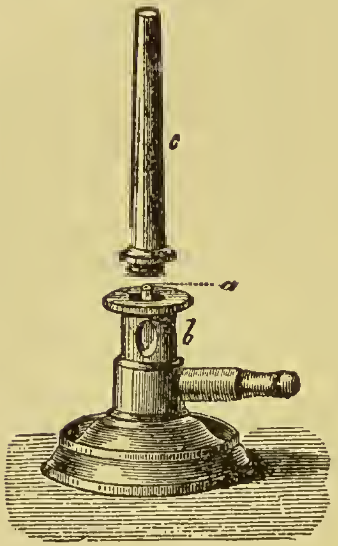


Fig. 80.

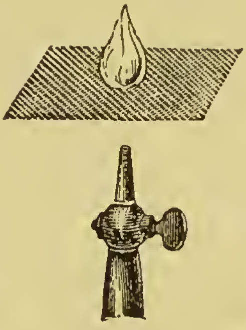
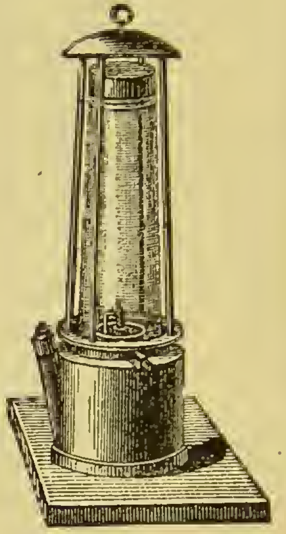


Fig. 81.



In rendering flame non-luminous by carbon dioxide, we must also consider that the same is converted, by the particles of carbon, into carbon monoxide:—

$$CO_2 + C = 2CO.$$

Indeed, but a few per cent. of CO_2 in a gas flame suffices to considerably diminish its luminosity,

$$\underset{\text{1 vol.}}{C_2H_4} + \underset{\text{1 vol.}}{CO_2} = \underset{\text{1 vol.}}{CH_4} + \underset{\text{2 vols.}}{2CO},$$

while the presence of nitrogen is far less detrimental.

Every substance requires a definite temperature for its ignition—*temperature of ignition.* When a substance is once ignited it generally burns further, because additional particles are raised to the temperature of ignition by the heat of combustion. By rapid cooling (*e.g.*, by the introduction of a piece of metal into a small flame) every flame may be extinguished. By holding a metallic net over the opening of a gas lamp, from which gas issues, and igniting the same above the wire (Fig. 80), the latter, being a good conductor of heat, cools the flame so much that it is incapable of igniting the gas below the gauze. Upon this phenomenon depends the construction of Davy's safety lamp, which is used in coal mines, to avoid ignition of the fire-damp (Fig. 81). It is an ordinary oil lamp surrounded and shut off from the air by a metallic wire gauze. On bringing a lighted lamp of this sort into an explosive mixture, or into a combustible gas (*e. g.*, into a large jar, in which ether is present), the gas penetrating into the lamp will burn, but the combustion will not extend to the external gases.

COMPOUNDS OF CARBON WITH THE HALOGENS.

Carbon does not combine directly with the halogens; the compounds result, however, by the action of the halogens upon the hydrocarbons. We have seen that chlorine and bromine act upon water, ammonia, H_2S, PH_3, etc., in such manner as to unite with the hydrogen to form hydrogen chloride, etc., while the other element is either set free or is also combined with the chlorine. Chlorine and bromine act similarly upon the hydrocarbons; here hydrogen is displaced, atom after atom, by chlorine, forming HCl and chlorine derivatives:—

$$\begin{aligned} CH_4 + Cl_2 &= CH_3Cl + HCl \\ CH_4 + 2Cl_2 &= CH_2Cl_2 + 2HCl \\ CH_4 + 3Cl_2 &= CHCl_3 + 3HCl, \text{ etc.} \end{aligned}$$

Such a process is termed *substitution*, and the products *substitution products*. In this way we obtain from methane, CH_4, the products, CH_3Cl, CH_2Cl_2, $CHCl_3$ (*chloroform*) and finally CCl_4, *carbon tetrachloride*. The last compound is a colorless, ethereal liquid, boiling at 76.7°. Its vapor density equals 76.9 ($H = 1$), corresponding to the molecular formula $CCl_4 = 153.8$. The chlorides of carbon are not decomposed by water.

The compound C_2Cl_6, *hexachlorethane*, obtained by the action of chlorine upon ethane, C_2H_6, is a crystalline mass, fusing and boiling at 188°. On conducting the vapors through a red-hot tube they decompose into C_2Cl_4 and Cl_2. *Ethylene tetrachloride*, C_2Cl_4, is a liquid, boiling at 122° C. Bromine and iodine yield similar compounds; they will be treated more extensively in organic chemistry.

The *heats of formation* of the previously mentioned hydrocarbons (from amorphous carbon and hydrogen) are deduced from the heat of combustion, and equal:—

$$(C,H_4) = 21.7;\ (C_2,H_6) = 28.6;\ (C_2,H_4) = -2.7;\ (C_2,H_2) = -48.3.$$

The absorption of heat in the formation of acetylene and ethylene is explained by the fact that the solid carbon molecules must first be gasified and separated into atoms in order to unite with hydrogen. The disgregation heat requisite for this equals very probably upward of 38.3 C., for 12 parts by weight of amorphous carbon (76.6 C. for 24 parts); then the preceding heats of formation must be enlarged about this much, in order to express the true heat of formation (from gaseous carbon atoms) of the hydrocarbons.

Beginning with acetylene, C_2H_2, we discover that its conversion into ethylene, C_2H_4, and into ethane, C_2H_6, ensues with heat disengagement:—

$$(C_2H_2,H_2) = 45.5; (C_2H_4,H_2) = 28.3.$$

In accordance with this acetylene readily unites with hydrogen (*in statu nascendi*, or by action of platinum sponge, etc.), forming ethylene and ethane.

The *heats of formation* of the carbon chlorides approach those of the hydrogen derivatives very closely:—

$$(C,Cl_4\text{—gas}) = 21.0; (C_2,Cl_4\text{—gas}) = -1.1.$$

The affinity of chlorine for carbon is, therefore, very nearly the same as that of hydrogen.

2. SILICON.

$Si = 28.4.$

Next to oxygen this is the most widely distributed element in nature. Owing to its affinity for the former it does not occur in a free condition. Combined with oxygen as silicon dioxide (SiO_2), and in the form of salts of silicic acid (silicates) it comprises many minerals and almost all the crystalline rocks.

It may be obtained in a free condition by heating silicon fluoride ($SiFl_4$), or sodium-silicon fluoride (Na_2SiFl_6) with metallic sodium:—

$$Na_2SiFl_6 + 4Na = 6NaFl + Si.$$

The ignited mass is treated with water, which dissolves the sodium fluoride and leaves the silicon as a brown, non-lustrous, *amorphous* powder. It burns to silicon dioxide (SiO_2) when heated in the air.

Another modification—the *crystalline silicon*—is obtained by fusing a mixture of Na_2SiFl_6, sodium and zinc. The separated silicon dissolves in the molten zinc, and on cooling, deposits out in crystals, which remain on dissolving the metal in hydrochloric acid. It can also be prepared as follows: 50 grams of magnesium powder are mixed with 200 grams of dry sea-sand, and the mixture heated in hard glass tubes over a blast lamp. The product of amorphous silicon is then pulverized, mixed with ten times its weight of zinc dust, and exposed to heat in a Hessian crucible until the zinc just commences to vaporize. After cooling, the zinc regulus is washed and dissolved in hydrochloric acid. The crystalline product consists of black, shining octahedra, of specific gravity 2.49, and of very great hardness. Upon ignition in the air or oxygen it is not oxidized; it is not attacked by acids. On boiling it with a sodium or potassium hydroxide solution it dissolves, forming a silicate and liberating hydrogen:—

$$Si + 4KOH = K_4SiO_4 + 2H_2.$$

Heated in chlorine gas, silicon burns to the chloride.

Hydrogen Silicide—SiH_4—the analogue of CH_4, is produced like arsine by dissolving an alloy of silicon and magnesium in dilute hydrochloric acid:—

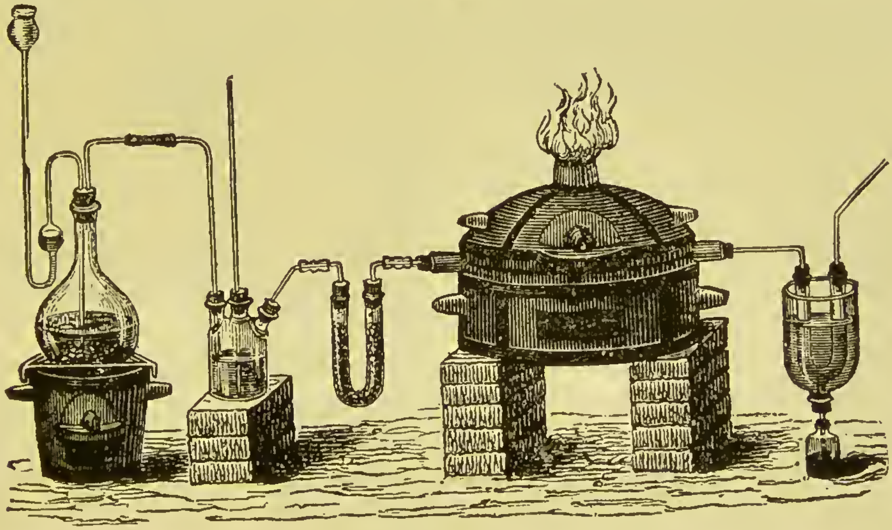
$$SiMg_2 + 4HCl = SiH_4 + 2MgCl_2.$$

The escaping hydride contains admixed hydrogen, has a disagreeable odor, ignites spontaneously in the air, and burns to the dioxide and water:—

$$SiH_4 + 2O_2 = SiO_2 + 2H_2O.$$

Perfectly pure silicide, free of H, is obtained by heating a compound, $SiH(O.C_2H_5)_3$, which will be treated in Organic Chemistry. In the air at ordinary pressure, it ignites only upon warming; if, however, the gas, by diminution of pressure or by the addition of H, is diluted, it becomes spontaneously combustible at ordinary temperatures. A red heat decomposes the hydride into amorphous silica and hydrogen. When mixed with chlorine it inflames and probably forms substitution products similar to those of methane (CH_4). Pure hydrogen silicide condenses to a liquid, at −5° and a pressure of 70 atmospheres.

FIG. 82.



Silicon Chloride—$SiCl_4$—results from the action of chlorine upon silicon, or by conducting chlorine over an ignited mixture of the dioxide and carbon (Fig. 82):—

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO.$$

The mixture is placed in a porcelain tube, which is heated to a red heat in a charcoal furnace. The chlorine generated in the flask is washed in a three-necked bottle and dried in a glass tube filled with calcium chloride. While carbon or chlorine do not act separately upon the SiO_2, when they act simultaneously the reaction is induced by the mutually supporting affinities of carbon for oxygen and of chlorine for silicon.

A simpler procedure consists in exposing the amorphous silicon that results upon heating sand with magnesium powder to the action of chlorine gas, while a *gentle* heat is applied in a combustion furnace. The chloride formed is very volatile and is condensed in a receiver surrounded by a freezing mixture of ice and salt (*Berichte*, 22, 188).

Silicon chloride is a colorless liquid, having a specific gravity of 1.52, and boiling at 57°. It fumes in the air, and is decomposed by water into silicic and hydrochloric acids:—

$$SiCl_4 + 4H_2O = H_4SiO_4 + 4HCl.$$

This compound may be employed in determining the atomic weight of silicon. Analysis shows that it contains seven parts silicon for every 35.45 parts of chlorine. Supposing, from the great analogy of the silicon compounds to those of carbon, that its formula is $SiCl_4$, the atomic weight of the silicon would be 28.4:—

$$\begin{array}{rcl} Si & = & 28.4 \\ Cl_4 & = & 141.80 \quad (4 \times 35.45). \\ \hline SiCl_4 & = & 170.2 \end{array}$$

This supposition is confirmed by the vapor density of the compound. This equals 84.7 ($H = 1$), hence the molecular weight is $2 \times 84.7 = 169.4$. As the analysis shows that there are 141.8 parts chlorine in 170.2 parts of silicon chloride, the atomic weight of the metal must be 28.4.

Silicon Bromide—$SiBr_4$—and **Silicon Iodide**—SiI_4—are formed in the same manner as the chloride. The first is a colorless liquid, of specific gravity 2.8, becoming solid at —12° and boiling at + 153°. The iodide forms colorless octahedra, fusing at 120°, and boiling at 290°. Like the chloride, both are decomposed by water.

Besides these compounds, which may be viewed as hydrogen silicide, in which all the hydrogen is replaced by halogens (see p. 161), others exist, in which only a part of this element is replaced. Thus, *silicon chloroform*, $SiHCl_3$, corresponds to the chloroform ($CHCl_3$) derived from methane. It is produced by the action of phosphorus pentachloride, or antimony chloride, on hydrogen silicide:—

$$SiH_4 + 3SbCl_5 = SiHCl_3 + 3SbCl_3 + 3HCl;$$

or upon heating silicon in dry hydrogen chloride gas: in this case a mixture of $SiCl_4$ and $SiHCl_3$ results (see also *Berichte*, 22, 188). These compounds may be separated by fractional distillation. Silicon chloroform is a colorless liquid, of specific gravity 1.6, and boils at 35°–37°. The vapor density equals 67.5 ($H = 1$), corresponding to the molecular formula, $SiHCl_3 = 135.11$. It fumes in the air, and decomposes with water into silicic and hydrochloric acids.

The silicon bromoform, $SiHBr_3$, and iodoform, $SiHI_3$, are very similar to chloroform; these correspond to the analogous carbon compounds.

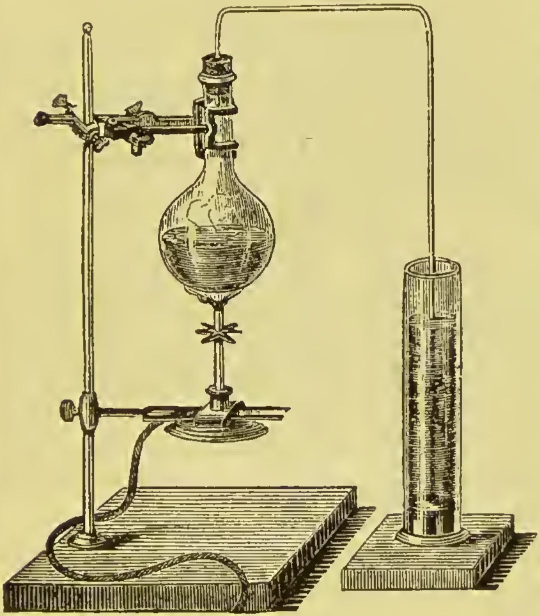
The compounds Si_2Cl_6 and Si_2I_6 are known. They correspond to C_2Cl_6. From all these data we observe the great analogy between silicon and carbon.

Silicon Fluoride, $SiFl_4$, is formed when HFl acts upon SiO_2:—

$$SiO_2 + 4HFl = SiFl_4 + 2H_2O.$$

To prepare it, a mixture of fluorite and powdered glass, or sand (SiO_2), is warmed with sulphuric acid; by the action of H_2SO_4 upon the fluorite hydrogen fluoride (p. 64) is disengaged, and this reacts upon the silicon dioxide, in the manner indicated in the above equation. The liberated gas is collected over mercury. It is colorless, has a disagreeable odor, and fumes strongly in the air. Its vapor density is 3.60 (air = 1), or 52 (H = 1), corresponding to the molecular formula $SiFl_4 = 104$. Its deportment with water is very characteristic; it is decomposed thereby into silicic acid (H_4SiO_4) and hydrogen silicofluoride: $3SiFl_4 + 4H_2O = H_4SiO_4 + 2H_2SiFl_6$. For the execution of this method, conduct the $SiFl_4$ formed, through a glass tube, into a vessel containing water (Fig. 83). Gelatinous silicic acid separates out, and the gaseous SiH_2Fl_6 remains dissolved in the water. As the separating silicic acid may easily obstruct the opening of the glass tube, the latter is allowed to project a slight distance into mercury. The solid silicic acid is separated from the aqueous solution by filtration.

FIG. 83.



Hydrogen Silico-Fluoride—H_2SiFl_6 (or $2HFl,SiFl_4$),—is only known in aqueous solution. Upon evaporating at a low heat it decomposes into $SiFl_4$ and 2HFl. In its chemical deportment it is an acid similar to the hydrogen-halogen acids. Its aqueous solution reddens blue litmus paper, dissolves many metals, and saturates bases, forming salts with them, in which two hydrogen atoms are replaced by metal.

The potassium and barium salts are insoluble in water.

The *heats of formation* of the halogen derivatives of silicon are as follows:—

$$(Si,Cl_4) = 157.6;\ (Si,Br_4)\ 120.4\ (Si,I_4) = 58.0.$$

These numbers readily account for their general behavior. And their ready decomposability by water may be accounted for if the heat of formation of silicic acid be considered ($SiO_2 = 219.0$ Cal.). Their deportment toward oxygen is also very interesting. The heat disengagement, in their transposition, following the equation,—

$$SiX_4 + O_2 = Si,O_2 + 4X,$$

equals 61.4 Cal., with the chloride, 98.6 Cal., with the bromides, and with the iodides 161.0 (219–58). Therefore, oxygen must liberate the halogen atoms present in them. And this occurs with the chloride and bromide when raised to a red-heat, while the iodide inflames in the air, yielding silicon dioxide and iodine vapor. This behavior accords with the great amount of heat which is set free. The halogen derivatives of arsenic and phosphorus react similarly.

TIN, Sn = 118.1, and the recently discovered GERMANIUM, Ge = 72.3, attach themselves in chemical character to the group containing carbon and silicon. They bear the same relation to the latter elements that arsenic and antimony bear to the members of the nitrogen group. This is evident in their atomic weights:—

N = 14.041   P = 31.03   As = 75   Sb = 120.3
C = 12   Si = 28.4   Ge = 72.3   Sn = 118.1.

Germanium and tin, like carbon and silicon, form volatile compounds with four atoms of the halogens, *e. g.*, $GeCl_4$ and $SnCl_4$. In a similar manner they unite with oxygen to yield dioxides, *e. g.*, GeO_2 and SnO_2, which resemble silicon dioxide in having an acid character. On the other hand, they do not form volatile hydrogen derivatives, and are thus markedly distinguished from the other non-metals. Therefore germanium and tin, with their higher analogue, LEAD, will be treated with the metals.

In the preceding pages we have considered four groups of elements, comprising all the so-called metalloids (with the exception of boron). In each group the last members, possessing the highest atomic weights, exhibit very distinct metallic properties, especially when in their free state. This is clearly the case with germanium, tin, antimony, and arsenic. Tellurium and selenium also (in the crystalline modification) possess marked metallic appearance; finally, iodine has a metallic lustre. The affinity for hydrogen, on the other hand, diminishes with increase in metallic character; the hydrides of iodine, tellurium, antimony, and arsenic, are very unstable, and decompose readily into their constituents; finally, tin and bismuth do not combine with hydrogen.

The remarkable relations between the atomic weights of the elements of the four groups are seen in the following table. The deportment of the elements is expressed by the same.

C = 12 N = 14.041 O = 16 Fl = 19
Si = 28.4 P = 31.03 S = 32.06 Cl = 35.453
Ge = 72.3 As = 75 Se = 79.1 Br = 79.963
Sn = 118.1 Sb = 120.3 Te = 125 I = 126.86.

We will give a fuller consideration of these relations in the presentation of the *Periodic System of the Elements.*

ATOM AND MOLECULE.

In the study of the hydrogen derivatives of the elements of the four groups already mentioned, we arrived at the establishment of the following formulas:—

CH_4.	NH_3.	OH_2.	FlH.
SiH_4.	PH_3.	SH_2.	ClH.
......	AsH_3.	SeH_2.	BrH.
......	SbH_3.	TeH_2.	IH.

These formulas possess a fundamental importance, and serve for the deduction of other more important conclusions and generalizations, and for this reason we again here introduce in a connected form all the actual relations and considerations that were the basis of their derivation.

The fact, proved by the analysis and synthesis of chemical bodies, that the elements combine with each other according to constant multiple proportions, is most simply explained by the supposition of elementary atoms, which can combine among themselves in different quantity (page 72). The existence of isomeric bodies can only be concluded from the atomic constitution of matter (p. 88). The experimental combining weights, however, offer no assistance in determining the number of atoms in a compound, and, therefore, the true relative atomic weights of the elements (p. 72); the question can only be solved upon a basis of other actual relations. The specific gravities of the bodies in the gaseous and vapor form, and the relations according to which the gases combine by volume render an important service in this task.

The physical properties of the gases and vapors lead to the supposition that they consist of very small discrete particles, molecules, which are separated from each other by relatively large but like distances, and that, therefore, an equal number of molecules is contained in equal volumes of all gases. *Hence molecules are the smallest particles of matter—masses—which occur separated in gases; their relative weights, therefore, are directly expressed by their relative gas densities* (p. 80). Molecules of compound bodies are composed of atoms; therefore, the relative atomic weights may be derived from the molecular weights. *The atomic weight is the smallest quantity of an element which is contained in the molecular weight of any one compound.* Although the atomic weights of the above considered elements have been deduced from a small number of compounds, yet all further investigations have confirmed the observation that these elements are not contained in a smaller quantity in any molecule. Thus oxygen is present in all molecules, in at least 16 parts by weight; nitrogen not less than 14.04; carbon not less than 12—if the smallest quantity of hydrogen contained in a molecule, *i. e.*, an atom, equals 1.

From a comparison of the densities of the elements with those of their derivatives we concluded (p. 77)—upon the basis of the proposition, that an equal number of molecules is contained in equal gas-volumes—that the molecules of the elements consist of two or more atoms. Thus the molecules of hydrogen, the halogens, oxygen, nitrogen, are composed of two atoms; the sulphur molecules at 500° of six atoms; the molecules of phosphorus and arsenic of four atoms:—

$$H_2 \quad Cl_2 \quad O_2 \quad N_2 \quad S_6 \quad P_4 \quad As_4.$$

The molecular quantities of all bodies in the gaseous state occupy equal volumes. Referring the densities (specific gravities) to hydrogen as a unit (= 1), the molecular weights are double the densities, and conversely, the latter are half the molecular weights (p. 79).

The existence of allotropic modifications of the elements confirms (p. 88) the hypothesis that the molecules of the elements are composed of several atoms. In the gaseous condition the allotropy is known only in the case of oxygen and sulphur. Ordinary oxygen has two atoms, ozone three; the sulphur molecule, at 1000°, contains two atoms; at 500°, however, six atoms. Although we possess no means of determining the molecular value of the solid elements, yet there are many indications that the free elements occurring in several modifications, like P, As, C, and Si, consist of complex groups of atoms.* Further, the energetic action of the elements in the moment of their formation (see p. 79) argues for their complexity when free.

The phenomena of the so-called *status nascens* find their explanation, in the majority of cases, in the thermo-chemical changes accompanying them. If, *e. g.*, in the action of zinc upon nitric acid, where, from analogy to other acids, hydrogen must be set free, the same does not occur, but the nitric acid is reduced to ammonia and nitrogen oxides—while free hydrogen does not exert any action on nitric acid—then it is the heat disengaged by the formation of zinc and ammonium nitrates, which, in accordance with the principle of greatest heat liberation, represents the true cause of the reaction. However, the supposition that the free atoms act more energetically than the molecules is not refuted by this; it finds an additional confirmation in thermo-chemistry.

---

* Recently it has been discovered that it is possible to determine the molecular magnitude of a substance in solution by the lowering of the melting point of its solvent (water, benzene).—Raoult (see Organic Chemistry). Hence, it appears that in a benzene solution the sulphur molecules consist of six atoms (S_6), and the phosphorus molecules of four and two atoms (P_4 and P_2) (Paternò).

The determination of the density is the simplest means of ascertaining the molecular quantity; but we have another, a purely chemical procedure, leading to the same end. As molecules are the smallest quantities which can exist in a free condition, it is very probable the same quantities appear in the chemical reactions. Indeed, the study of the latter leads us to the same molecular quantities as are derived from the densities. For example, the compound CH_3Cl results when chlorine acts upon marsh gas; we hence infer that four atoms of H are present in the molecule of the latter hydrocarbon:—

$$CH_4 + Cl_2 = CH_3Cl + HCl.$$

From ethylene—C_2H_4—we obtain C_2H_3Cl; the composition of the former, therefore, cannot be expressed by the simpler formula, CH_2. With iodine, ammonia yields NHI_2; with hydrogen chloride NH_4Cl:—

$$\begin{aligned} NH_3 + 2I_2 &= NHI_2 + 2HI. \\ NH_3 + HCl &= NH_4Cl. \end{aligned}$$

Both reactions prove that three atoms of hydrogen are present in ammonia. The compound nature of the elementary molecules is concluded in the same manner; in all accurately determined reactions we perceive that hydrogen, the halogens, oxygen, nitrogen, invariably act or separate out with two atoms, as is observed from the following equations:—

$$\begin{aligned} MnO_2 + 4HCl &= MnCl_2 + 2H_2O + Cl_2, \\ NH_4NO_2 &= 2H_2O + N_2, \\ Ag_2O + H_2O_2 &= Ag_2 + H_2O + O_2. \end{aligned}$$

Although this chemical method for obtaining the molecular value is less simple, it is much more general than the one depending on the determination of the densities, because it can be applied in the case of the non-volatile bodies. Thus, for example, the composition of hydrogen peroxide is expressed by the formula, HO; the methods of its production and chemical rearrangements point, however, with great probability, to the doubled molecular formula, H_2O_2.

Hence the most varied relations carry us to the same conclusions as to the existence and the quantity or value of the atoms and molecules. The atomic-molecular formulas used in chemistry to-day are only the expression of actual relations; they are entirely independent of speculative abstractions, but forcibly call out these.

THE VALENCE OF THE ELEMENTS. CHEMICAL STRUCTURE.

Important generalizations result from the molecular formulas deduced above. We have the four following groups of hydrogen compounds (forms of combination or types):—

CH_4	NH_3	OH_2	FlH
SiH_4	PH_3	SH_2	ClH
......	AsH_3	SeH_2	BrH
......	SbH_3	TeH_2	IH

In each group the affinity of the elements for hydrogen diminishes, step by step, with increasing atomic weight. Yet the number of hydrogen atoms which are combined with *one* atom of the other elements is constant for each group. Hence, we must ascribe a particular function of affinity to each element, in its relation to hydrogen. This is called its *valence* or *atomicity.* The elements of the fluorine group are univalent or monatomic; the elements of the oxygen group *bivalent or diatomic;* nitrogen and its analogues, *trivalent;* carbon and silicon, finally, are *tetravalent* elements—if we accept the valence of hydrogen as the *unit of valence.* The halogens, combining with *one* atom of hydrogen, possess *one affinity unit;* oxygen combines with two hydrogen atoms, and possesses, therefore, *two* affinity units, etc.

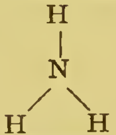
The valence of the elements is frequently designated by lines or Roman numerals placed above the symbols:—

$$\overset{\text{I}}{\text{Cl}} \qquad \overset{\text{II}}{\text{O}} \qquad \overset{\text{III}}{\text{N}} \qquad \overset{\text{IV}}{\text{C}}.$$

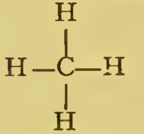
The mutual union of affinity units is indicated by one line:—

H—Cl
Hydrogen chloride.

H—O—H
Water.



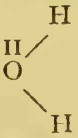
Ammonia.



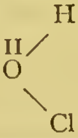
Methane.

In these formulas the atoms of oxygen, of nitrogen, of carbon—indeed, of all the multivalent elements—represent, as it were, the nuclei to which the hydrogen atoms attach themselves; their valence units are, as it were, the points of attachment for the valence unit of hydrogen.

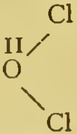
The hydrogen atoms in these molecules can be replaced or substituted by other elements (p. 161). According to this, the monovalent halogen atoms each replace one hydrogen atom:—



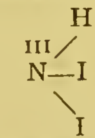
Water.



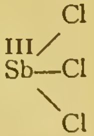
Hypochlorous acid.



Chlorine oxide.



Nitrogen iodide.

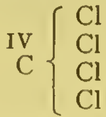


Antimony trichloride.

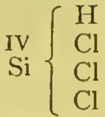
It is more convenient to employ brackets instead of the lines:—


$\overset{IV}{C}\left\{\begin{matrix}H\\Cl\\Cl\\Cl\end{matrix}\right.$

Chloroform.


$\overset{IV}{C}\left\{\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}\right.$

Carbon tetrachloride.


$\overset{IV}{Si}\left\{\begin{matrix}H\\Cl\\Cl\\Cl\end{matrix}\right.$

Silicon chloroform.

By the replacement of hydrogen in the preceding hydrogen compounds by the monovalent metal potassium, we obtain

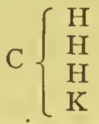
K—Cl

Potassium chloride.

Potassium hydroxide.

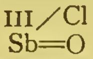

$N\left\{\begin{matrix}H\\K\\K\end{matrix}\right.$

Di-pot. amide.

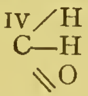

$C\left\{\begin{matrix}H\\H\\H\\K\end{matrix}\right.$

Potassium methyl.

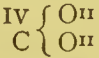
The bivalent elements, like oxygen, sulphur, replace two hydrogen atoms in the compounds of that element:—



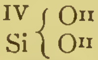
Antimony oxychloride.



Methylene oxide.


$\overset{IV}{C}\left\{\begin{matrix}O^{II}\\O^{II}\end{matrix}\right.$

Carbon dioxide.


$\overset{IV}{Si}\left\{\begin{matrix}O^{II}\\O^{II}\end{matrix}\right.$

Silicon dioxide.

Finally, trivalent nitrogen can replace three atoms of hydrogen, or three of the halogens:—


$\overset{IV}{C}\left\{\begin{matrix}\overset{III}{N}\\H\end{matrix}\right.$

or, $\overset{I}{H}—\overset{IV}{C}\equiv\overset{III}{N}$

Hydrogen cyanide.


$\overset{IV}{C}\left\{\begin{matrix}\overset{III}{N}\\Cl\end{matrix}\right.$

or, $\overset{I}{Cl}—\overset{IV}{C}\equiv\overset{III}{N}$

Chlorcyanogen.

In all these compounds we have that valence appearing which is peculiar to the elements themselves.

Like valence is designated by the word *equivalence*. One atom of chlorine is equivalent to one atom of hydrogen; 35.45 parts, by weight, of chlorine are, then, equivalent to 1 part, by weight, of hydrogen. One atom of oxygen is equivalent to two atoms of hydrogen; consequently, 2 parts, by weight, of hydrogen are equivalent to 16 parts, by weight, of O, or 1H to 8 parts of oxygen. Further, 1 atom of N, or 14 parts, is equivalent to 3 atoms or 3 parts hydrogen; 1 part hydrogen is, therefore, equivalent to $\frac{14}{3} = 4.66$ parts nitrogen, etc. These quantities, equal to 1 part, by weight, of H, are termed *equivalent weights*, and were formerly employed instead of the atomic weights. As may be observed from the preceding, the equivalent weights are parts of the atomic weights corresponding to the valence units of the atoms.

If, consequently, the valence of the elements, in relation to hydrogen (as also to other elements), has a definite value, the question naturally arises—what will result if an atom of hydrogen be withdrawn from the saturated molecules, *e. g.*, water, H_2O, ammonia, NH_3, or methane, CH_4? The resulting *groups* or *residues*—

$-\overset{\text{II}}{O}-H$	$-\overset{\text{II}}{S}-H$	$-\overset{\text{III}}{N}=H_2$	$-\overset{\text{IV}}{C}\equiv H_3$
Hydroxyl.	Sulphydrate.	Amide.	Methyl.

can plainly not exist in a free condition, as the one affinity unit of the element having higher valence, is not saturated. When set free, these groups, therefore (like the elementary atoms), unite with the free affinities and enter into complicated compounds. Thus, for example, we obtain the bodies—

$H\overset{\text{II}}{O}-\overset{\text{II}}{O}H$	$H\overset{\text{II}}{S}-\overset{\text{II}}{S}H$	$H_2\overset{\text{III}}{P}-\overset{\text{III}}{P}H_2$	$H_3\overset{\text{IV}}{C}-\overset{\text{IV}}{C}H_3$
Hydrogen peroxide.	Hydrogen persulphide.	Liquid hydrogen phosphide.	Dimethyl or ethane.

Carbon is particularly inclined to such combination. Upon removing an atom of H from dimethyl or ethane (C_2H_6) the so-called ethyl group remains:—

$$C_2H_5 \text{ or } \overset{\text{IV}}{C}H_3-\overset{\text{IV}}{C}H_2-$$

in which one carbon affinity is unsaturated; this can again unite with the methyl group CH_3. The resulting compound is:—

$$C_3H_8 \text{ or } H_3\overset{\text{IV}}{C}-\overset{\text{IV}}{C}H_2-\overset{\text{IV}}{C}H_3, \text{ or } C_2H_5.\,CH_3.$$

By the continuation of this process of a chain-like union, as it were, of the carbon atoms, we obtain a whole series of hydrocarbons (C_4H_{10}, C_5H_{12}, etc.) with the general formula C_nH_{2n+2} (compare page 155).

Not only similar residues or groups, but dissimilar also, combine in this way:—

$H_2\overset{\text{III}}{N}-\overset{\text{II}}{O}H$	$H_3\overset{\text{IV}}{C}-\overset{\text{II}}{O}H$	$H_3\overset{\text{IV}}{C}-\overset{\text{III}}{N}H_2.$
Hydroxylamine.	Methyl hydroxide.	Methylamine.

Such combinations are generally effected by reactions of double decomposition. Thus methyl hydroxide (wood-spirit) results from the action of methyl iodide (CH_3I) upon silver hydroxide ($AgOH$):—

$$CH_3I + AgOH = AgI + CH_3OH;$$

methylamine by the action of methyl iodide and ammonia:—

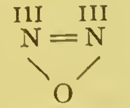
$$CH_3I + NH_3 = CH_3NH_2 + HI.$$

Dimethyl is produced when sodium acts upon methyl iodide:—

$$2CH_3I + Na_2 = 2NaI + C_2H_6.$$

By the withdrawal of iodine the methyl groups are liberated, and then combine with each other.

Further, the atoms with several valences can unite with two and three affinities (*double* and *triple* union) :—



Hyponitrous oxide.

$\overset{IV}{H_2C} = \overset{IV}{CH_2}$
Ethylene.
(p. 155.)

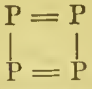
$\overset{IV}{HC} \equiv \overset{IV}{CH}$
Acetylene.
(p. 156.)

By complete mutual union result the free elements :—

$H - H$
Hydrogen.

$O = O$
Oxygen.

$N \equiv N$
Nitrogen.



Phosphorus.

This manner of linking or combination of the atoms in the molecule, not with their entire mass but with single affinities, is designated *chemical constitution* or *chemical structure* of compounds; the formulas representing them are called *constitution* or *structural formulas*. Of course the actual position of the atoms in space (of which we have no knowledge) is not indicated by the chemical structure. The fundamental principle of chemical structure consists in this, that *the affinity unit of one atom unites itself with the affinity unit of another atom*. The following circumstances, however, complicate these simple relations: Among the elements of the nitrogen group we saw that P and N combine with 3 and 5 atoms of chlorine and the other halogens; that sulphur, selenium, and tellurium take up 2 and 4 atoms of chlorine and bromine; that iodine unites with 1 and 3 atoms of chlorine and 5 of fluorine. Only the tretravalent elements, carbon and silicon, are capable of combining with 4 hydrogen atoms, and with not more than 4 of the halogens :—

$\overset{IV}{CCl_4}$	$\overset{III}{PCl_3}$	$\overset{II}{SCl_2}$	$\overset{I}{ICl}$
......	$\overset{V}{PCl_5}$	$\overset{IV}{SCl_4}$	$\overset{III}{ICl_3}$
......	......	......	$\overset{V}{IFl_5}$

Hence, it appears that the elements (excepting carbon) do not express such a constant valence in their relation to chlorine (and to the halogens) as they do to hydrogen. P and its analogues appear to be tri- and pentavalent; the elements of the sulphur group, di- and tetravalent; iodine finally appears to be mono-, tri-, and pentavalent.

This higher valence of the metalloids shows itself more distinctly and frequently in the more stable oxygen derivatives. We are acquainted with the following oxygen compounds of the elements of the four groups already mentioned; the members of each group afford perfectly analogous compounds :—

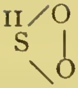
IV CO_2	III N_2O_3	II (SCl_2)	I Cl_2O
......	V N_2O_5	IV SO_2	III Cl_2O_3
......	......	VI SO_3	V I_2O_5
......	......	......	VII I_2O_7

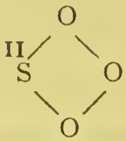
Hence the valence of iodine (and of the halogens) reaches seven, and the elements of the sulphur group six affinity units. The elements of the nitrogen group are not more than pentavalent, both in their relation to chlorine and oxygen. Carbon, finally, does not show more than four affinities for H, Cl, or O. As we will observe later, these relations are more apparent in the hydroxyl derivatives of the oxides, the acids. Hence we conclude, *that valence is not an absolute property belonging per se to and for the elements solely* (*like the atomic weights*) but that *it appears as a function of the mutual action of the various elements.* We can, in general, distinguish two valences; the *hydrogen valence* and the *halogen* or *oxygen valence.* The hydrogen valence is *constant* for all elements; for Cl = 1, for O = 2, for N = 3, for C = 4. The valence of the most of the elements appears to be *variable* in respect to oxygen and chlorine. It varies, indeed, as seen from the formulas given above for the Cl group from 1 to 3 to 5 and to 7; for the elements of the S group from 2 to 4 to 6; for P and its analogues from 3 to 5. The regular increase of the maximum valence from C = 4 to Cl = 7 argues for the actual occurrence of a change of valence. It is perfectly immaterial whether we ascribe a variable valence to the elements or accept the maximum as the true measure, and regard the lower compounds as *unsaturated,* because we possess no conceptions upon the nature of valence. Later, we will discover that this alteration of valence finds full expression and generalization in the periodic system of the elements, which is based upon the grouping of the elements according to their atomic weights.

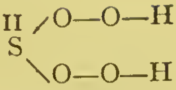
In the manner just represented, the idea of valence is viewed from a purely empirical standpoint. Another opinion prevails. This, denying the alterability, regards the *valence as an absolute constant property of the elementary atoms.* According to this idea, the true valence, or atomicity, is only derivable from the hydrogen compounds; the halogens are absolutely monovalent, the elements of the O group divalent, and those of the N group trivalent, etc. Different suppositions are proposed in order to carry out the constant atomicity for all compounds. A chain like union is assumed in order to explain the oxygen compounds. This is similar to the C atoms in the carbon compounds. It is represented in the following examples:—

$$\overset{I}{Cl}-\overset{II}{O}-\overset{II}{O}-\overset{II}{O}-\overset{I}{Cl} \qquad \overset{I}{Cl}-\overset{II}{O}-\overset{II}{O}-\overset{II}{O}-\overset{II}{O}-\overset{I}{H}$$

Chlorine trioxide. Perchloric acid.


Sulphur dioxide.


Sulphur trioxide.


Sulphuric acid.

$$\overset{II}{O}=\overset{III}{N}-\overset{II}{O}-\overset{II}{O}-\overset{II}{O}-\overset{III}{N}=\overset{II}{O}$$

Nitrogen pentoxide.

$$\overset{II}{O}=\overset{III}{N}-\overset{II}{O}-\overset{II}{O}-\overset{I}{H}$$

Nitric acid.

Hence it would appear that the oxygen atoms can unite without end, in a chain-like manner, similar to the C atoms in the carbon compounds. However, a maximum combining affinity of different groups for oyxgen does actually occur; this varies regularly from group to group (for $Cl = 7$, for $S = 6$, for $N = 5$, for $C = 4$). Consider it as we may, on the supposition of constant affinity, the reason for the different number of linking O atoms must be based on the nature of the other element. The fact, then, that the highest oxides or their hydrates ($HClO_4$, H_2SO_4, HNO_3) are more stable than the lower (p. 185), argues decidedly against the chain-like union of the oxygen atoms, such as occurs in the unstable peroxides.

To explain the other compounds according to the constant atomicity theory, a difference is conceived between *atomic* and *molecular* compounds. The former are such as can be explained by constant atomicity. All others are regarded as molecular compounds, resulting from the union of two or more molecules, upon the basis of newly acquired molecular affinities. Thus the compounds PCl_5, SCl_4, ICl_3, are viewed as addition products of atomic compounds with chlorine molecules:—

PCl_3, Cl_2	SCl_2, Cl_2	ICl, Cl_2.
Phosphorus pentachloride.	Sulphur tetrachloride.	Iodine trichloride.

It was thought that a proof that these bodies were differently constituted from the real atomic compounds, was seen in the fact that when vaporized they decomposed into simpler derivatives; the molecular compounds were not regarded as capable of existing as such in the gaseous state. We saw, however, that the decomposition of the molecules PCl_5, and SCl_4 is only gradual, increasing with the temperature, and that they do exist at lower temperatures, undecomposed, in a vapor form (compare p. 141). True atomic compounds, like H_2SO_4 and HNO_3, frequently separate into simpler molecules, in their conversion into vapor (compare Sulphuric Acid).

Phosphorus pentafluoride, PFl_5, a gas at ordinary temperatures, is a strong argument in favor of the pentavalence of phosphorus; iodine, too, affords a volatile pentafluoride, IFl_5. It is noteworthy that, as a general thing, the metalloids yield more stable and higher compounds with the lower halogens (fluorine and chlorine) than with bromine and iodine, which possess higher atomic weights (p. 54). The idea that molecular compounds can also exist in vapor form, would render their distinction from the atomic compounds purely arbitrary—not present in the nature of the bodies themselves. But other gaseous compounds exist, which can, in no light, be regarded as molecular. Thus, the usually tetravalent or hexavalent tungsten (WCl_6, $WOCl_4$) forms a gaseous pentachloride, WCl_5, and molybdenum, perfectly analogous to tungsten, yields a pentachloride, $MoCl_5$. Further, the pentavalent vanadium ($VdOCl_3$) gives rise to a gaseous tetrachloride, $VdCl_4$.

The salts of ammonia, according to the theory of constant atomicity, are not regarded as ammonium compounds,

$$\overset{V}{N}H_4Cl,\ \overset{V}{N}O_3NH_4,\ SO_4(\overset{V}{N}H_4)_2,$$

(p. 129), but as addition products of ammonia with acids,

$$NH_3,HCl,\quad NH_3,NO_3H,\quad (NH_3)_2,SO_4H_2,$$

which would make the analogy of the same with metallic salts appear rather doubtful. Further, the properties of many compounds like

$$\overset{V}{P}OCl_3,\ (C_2H_5)_3\overset{V}{P}O,\ (CH_3)_3\overset{IV}{S}.OH,\ (CH_3)_2\overset{IV}{S}O,\ (CH_3)_4\overset{V}{N}.OH,$$

and others, cannot be interpreted by the constant valence theory. The existence of potassium permanganate, MnO_4K, is not compatible with a constant di- or tetravalence of manganese.

Yet, up to the present, the acceptance of molecular additions could not be entirely dispensed with, especially for the so-called water of crystallization compounds; the proposed effort, however, continues to reduce all such compounds on the basis of higher valence of the elements. While, consequently, the constant valence theory comprises only the so-called atomic compounds, the extended valence idea draws all others into the circle of generalization.

We must, first of all, remember that the nature of chemical union and the cause of the valence of the atoms are entirely unknown to us, and that, therefore, neither the idea of a variable, nor yet of a constant valence constitutes a final explanation. So long as we do not possess an hypothesis upon the real causes, our task is restricted to collecting the varying combination relations of atoms into single points of view. The supposition of a constant valence, formerly given preference as the simpler, has shown itself to be insufficient. Because it maintains real differences, where such are not perceptible, it departs from the ground of induction. The idea of a variable valence, which takes all facts into consideration, is not prejudicial. Indeed, it finds a pregnant analogy in the deportment of the hydrocarbon radicals. By the elimination of hydrogen from the saturated molecules (C_2H_6, for example), we obtain radicals or groups of increasing valence (C_2H_5, C_2H_4, C_2H_3, C_2H_2, ...), just as the valence increases from fluorine to carbon ($Fl = 19$; $O = 16$; $N = 14$; $C = 12$). The group C_2H_2, however, is bi- and tetravalent; the group C_2H_3, mono- and trivalent. Everything, however, indicates that the chemical elements do not represent final individuals, but are composed of one or several primordial substances.

The principles of chemical structure, presented above, show themselves most distinctly, and with the greatest regularity, with carbon. The constitution of the innumerable varieties of carbon compounds is explained by the tetravalent nature of the carbon atoms, and their ability to combine with each other by single affinities. In the other, the so-called inorganic compounds, the valence and structure relations are more complicated, and are far less investigated, but even in them so many regularities show themselves that the actual material is greatly simplified thereby, and is made more comprehensible. The doctrine of valence and structure is the first attempt to refer the facts underlying the law of multiple proportions to the functions of the elementary atoms. As this theory only comprises actual relations, it cannot be negatived, but only further developed.

The foundation of the theory of atomicity and structure was laid down by A. Kekulè (1857–1859). It constitutes a representation and further development of the type theory of Gerhardt, at the basis of which lay, unrecognized, the idea of the different valence of the atoms.

OXYGEN COMPOUNDS OF THE METALLOIDS.

Almost all the oxygen derivatives of the metalloids are of an acid-forming nature; with water they yield acids:—

$$\underset{\text{Iodine heptoxide.}}{I_2O_7} + H_2O = \underset{\text{Periodic acid.}}{2HIO_4}; \quad \underset{\text{Sulphur trioxide.}}{SO_3} + H_2O = \underset{\text{Sulphuric acid.}}{H_2SO_4};$$

$$\underset{\text{Phosphorus pentoxide.}}{P_2O_5} + 3H_2O = \underset{\text{Phosphoric acid.}}{2H_3PO_4}.$$

Conversely, these oxides may be obtained by the removal of water from the acids; therefore, they are ordinarily termed *anhydrides* of the corresponding acids: I_2O_7—anhydride of periodic acid; SO_3—sulphuric anhydride; P_2O_5—phosphoric anhydride, etc.

Salts are formed by the replacement of the hydrogen of the acids by metals. The acids are distinguished as *monobasic*, *dibasic*, *tribasic*, or monohydric, dihydric, trihydric, etc., depending upon the number of their hydrogen atoms replaceable by metals.

Like the metalloids, the metals possess different valences; the monovalent metals (Na, K, Ag), replace each *one* hydrogen atom; those of higher valence replace more. Therefore the metals of higher valence can unite several acid residues. This explains the import, *e. g.*, of the following chemical formulas:—

$$\underset{\text{Potassium sulphate.}}{K_2SO_4} \qquad \underset{\text{Potassium sodium sulphate.}}{SO_4KNa} \qquad \underset{\text{Calcium sulphate.}}{SO_4\overset{II}{Ca}}$$

$$\underset{\text{Potassium nitrate.}}{NO_3K} \qquad \underset{\text{Copper nitrate.}}{(NO_3)_2\overset{II}{Cu}} \qquad \underset{\text{Bismuth nitrate.}}{(NO_3)_3\overset{III}{Bi}}$$

The salts of sulphuric acid are called *sulphates*, those of nitric acid, *nitrates*, those of phosphoric acid, *phosphates*, etc. The symbols of the metals are sometimes written at the beginning and sometimes at the end of the chemical formulas of the salts; in the second case we mean to indicate that the metal atoms are in union with the oxygen.

OXYGEN COMPOUNDS OF THE HALOGENS.

Excepting fluorine, all the halogens combine with oxygen to form anhydrides and acids which are analogously constituted, although not all the members are known for each halogen. The acids have *one* atom of hydrogen that can be replaced by metals, and hence are *monobasic*. Chlorine forms the following anhydrides and acids :—

Anhydrides.	Acids.
Cl_2O	$HClO$ — Hypochlorous acid.
Cl_2O_3	$HClO_2$—Chlorous acid.
(Cl_2O_5)	$HClO_3$—Chloric acid.
(Cl_2O_7)	$HClO_4$—Perchloric acid.

The anhydrides Cl_2O_3, Cl_2O_5, and Cl_2O_7 (corresponding to the compounds I_2O_5 and I_2O_7) are unknown. The compound Cl_2O_4 exists, and must be regarded as a mixed anhydride of chlorous and chloric acids.

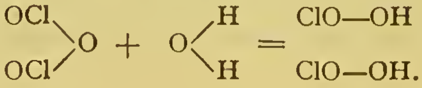
The following formulas express the chemical structure of these compounds :—

$\overset{I}{Cl}—\overset{II}{O}—\overset{I}{Cl}$ Hypochlorous anhydride.	$\overset{I}{Cl}—\overset{II}{O}—H.$ Hypochlorous acid.
$O\overset{III}{Cl}—O—\overset{III}{Cl}O$ Chlorous anhydride.	$(\overset{III}{Cl}O)—OH.$ Chlorous acid.
$O_2\overset{V}{Cl}—O—\overset{V}{Cl}O_2$ Chloric anhydride.	$(\overset{V}{Cl}O_2)—OH.$ Chloric acid.
$O_3\overset{VII}{Cl}—O—\overset{VII}{Cl}O_3$ Perchloric anhydride.	$(\overset{VII}{Cl}O_3)—OH.$ Perchloric acid.

$$O\overset{III}{Cl}—O—\overset{V}{Cl}O_2.$$

Chlorous-chloric anhydride.

In the acids we assume the presence of the monovalent group OH (hydroxyl or water residue) in which hydrogen can be replaced by metals, by the action of metals or bases. The group (ClO_2 or ClO_3) combined with hydroxyl is called an *acid residue* or *radical.* In the anhydrides two acid radicals are united by an oxygen atom ; water converts them into 2 molecules of acid :—



The salts of perchloric acid are called *perchlorates;* those of chloric acid, *chlorates;* those of chlorous acid, *chlorites;* and those of hypochlorous acid, *hypochlorites.*

Hypochlorous Oxide—Cl_2O—Hypochlorous anhydride, is produced by conducting dry chlorine gas over precipitated mercuric oxide, previously dried and heated to 250°. During the action of the chlorine, the oxide is cooled by ice or cold water:—

$$HgO + 2Cl_2 = HgCl_2 + Cl_2O.$$

The disengaged gas is condensed in a bent glass tube, cooled by a freezing mixture.

Hypochlorous oxide is a reddish-brown liquid, boiling at +5°. In the gaseous condition it has a yellow-brown color, an extremely disagreeable odor, and it attacks the respiratory organs very strongly. The vapor density is 43.45 ($H = 1$), corresponding to the formula, $Cl_2O = 86.9$. The gaseous or liquid oxide is very unstable and explosive. If heated, or if brought in contact with a flame, or exposed to the action of the electric spark, it decomposes with detonation into oxygen and chlorine:—

$$\underset{\text{2 vols.}}{2OCl_2} = \underset{\text{1 vol.}}{O_2} + \underset{\text{2 vols.}}{2Cl_2}$$

It is similarly exploded when it is brought into contact with sulphur, phosphorus, and organic substances, such as caoutchouc. It has strong oxidizing and bleaching properties. It dissolves in water to hypochlorous acid:—

$$Cl_2O + H_2O = 2HOCl.$$

It yields calcium hypochlorite and chlorine when it is conducted over porous calcium chloride:—

$$CaCl_2 + 2OCl_2 = Ca(OCl)_2 + 2Cl_2.$$

Hypochlorous Acid—$HClO$—is only known in aqueous solution. It is obtained by conducting chlorine into water in which there is suspended freshly precipitated mercuric oxide; the solution can be distilled. The concentrated solution is yellow in color, and is decomposed by light. It oxidizes and bleaches energetically. The bleaching action of this acid, due to the separation of oxygen *in statu nascendi*, is twice as great as that of free chlorine, as is evident from the following equations:—

$$Cl_2 + H_2O = 2HCl + O$$
$$2ClOH = 2HCl + O_2.$$

Hydrochloric acid decomposes hypochlorous acid into chlorine and water:—

$$ClOH + HCl = Cl_2 + H_2O.$$

The acid itself is very feeble and incapable of decomposing carbonates. Its salts (Bleaching powder, see Chloride of Lime) are formed by the action of chlorine, in the cold, upon strong bases:—

$$2NaOH + Cl_2 = NaCl + NaOCl + H_2O.$$

Upon heating their solutions with dilute nitric acid the free acid distils over.

On shaking the aqueous solution of hypochlorous acid with mercury, there is produced a white precipitate of $HgO.HgCl_2$, soluble in hydrochloric acid (salts of hypochlorous acid form HgO). This behavior serves to distinguish hypochlorous acid from chlorine, which under like circumstances forms Hg_2Cl_2, insoluble in hydrochloric acid (Reaction of Wolter).

Chlorine Trioxide—$Cl_2O_3 = (ClO)_2O$, the anhydride of chlorous acid (p. 178), and the free **Chlorous Acid**, $ClO_2H = ClO.OH$, are unknown. It was formerly supposed that the trioxide resulted by the reduction of chloric acid, if potassium chlorate, $KClO_3$, was decomposed by nitric acid in the presence of reducing substances (arsenic trioxide, sugar and tartaric acid). Later research has, however, shown that in such decompositions it is not the trioxide, but the dioxide, ClO_2, mixed with some chlorine and oxygen, that results.

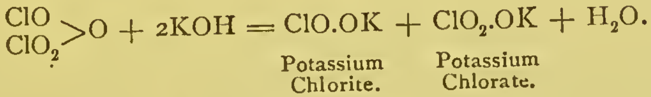
The salts of chlorous acid, the *chlorites*, *e. g.*, potassium chlorite, are formed by the transposition of the aqueous solution of chlorine dioxide with the alkalies (see below). The *silver salt*, ClO_2Ag, and the *lead salt*, $(ClO_2)_2Pb$, are precipitated from the aqueous solutions of the alkali salts by silver nitrate and lead acetate. They dissolve with difficulty in cold water, and crystallize from hot water in yellowish green scales.

Chlorine Dioxide, ClO_2, or **Chlorine Tetroxide**, Cl_2O_4, is formed when sulphuric acid acts in the cold upon potassium chlorate. It is best obtained (mixed with carbon dioxide) by adding dilute sulphuric acid (with 2 parts water) to a mixture of potassium chlorate and oxalic acid. Upon the application of a gentle heat a yellow-green gas escapes. It can be condensed by a freezing mixture to a reddish-brown liquid, boiling at 9.9° (under a pressure of 740 mm.). This liquid may be distilled from glass vessels, free from organic matter, if the temperature does not exceed 30° and does not undergo decomposition. Violent explosions occur at higher temperatures, so that it is advisable, if proper precautions are not taken, not to pour sulphuric acid upon potassium chlorate. Liquid as well as gaseous chlorine dioxide is very explosive, especially in contact with organic matter and when heated, but sunlight is without effect.

The formation of the oxide can be effected in a perfectly harmless way, and its powerful oxidizing action be illustrated, by throwing some potassium chlorate and a few pieces of yellow phosphorus into water, contained in a measuring glass, then allowing sulphuric acid to touch the bottom of the tube, drop by drop, by means of a pipette. By the action of the disengaged dioxide the phosphorus will burn under water with a brilliant light.

When concentrated sulphuric acid is added to a mixture of potassium chlorate and sugar, a violent combustion occurs.

Chlorine dioxide dissolves in water with a yellow color. Alkalies decolorize the solution, forming salts of chloric and chlorous acids:—

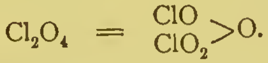


$$\begin{matrix}ClO\\ClO_2\end{matrix}{>}O + 2KOH = \underset{\text{Potassium Chlorite.}}{ClO.OK} + \underset{\text{Potassium Chlorate.}}{ClO_2.OK} + H_2O.$$

Sunlight decomposes the aqueous solution of chlorine dioxide into chloric acid, oxygen, and chlorine:—

$$3ClO_2 + H_2O = 2ClO_2.OH + O + Cl.$$

The gas density of the dioxide at + 10° has been found to equal 34.5, corresponding to the molecular formula ClO_2. It is, however, very probable that, at lower temperatures, in the liquid condition or in aqueous solution, the molecules possess the doubled formula, Cl_2O_4, and that then the compound represents the mixed anhydride of chloric and chlorous acids:—



$$Cl_2O_4 = \begin{matrix}ClO\\ClO_2\end{matrix}{>}O.$$

The decomposition of its aqueous solution by alkalies is an argument in favor of this view, as is also its analogy with nitrogen dioxide, NO_2, or nitrogen tetroxide, N_2O_4 (see this), the existence of both of which molecules has been proved.

Chloric Acid—$HClO_3$, or $ClO_2.OH$—is obtained by decomposing an aqueous solution of barium chlorate with sulphuric acid:—

$$\underset{\text{Barium chlorate.}}{(ClO_3)_2\overset{''}{Ba}} + SO_4H_2 = \underset{\text{Barium sulphate.}}{BaSO_4} + 2HClO_3.$$

The barium sulphate separates as a white, insoluble powder, and can then be filtered off from the aqueous solution of the acid. This is concentrated, under an air-pump, until the specific gravity becomes 1.28, and it then contains about 40 per cent. of chloric acid; it is oily and, when heated to 40°, decomposes into chlorine, oxygen, and perchloric acid, $HClO_4$. The concentrated aqueous solution oxidizes strongly; sulphur, phosphorus, alcohol, and paper, are inflamed by it. Hydrochloric acid eliminates chlorine from the acid and its salts:—

$$HClO_3 + 5HCl = 3H_2O + 3Cl_2.$$

The chlorates are produced, together with chlorides, by the action of chlorine, in the presence of heat, upon many bases (compare potassium chlorate):—

$$6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O.$$

Perchloric Acid—$HClO_4$, or $ClO_3.OH$. This is the most stable of all the oxygen derivatives of chlorine. As previously stated, it is produced by the decomposition of chloric acid, but is more easily obtained from its salts. Upon heating potassium chlorate to fusion, oxygen escapes and potassium perchlorate results:—

$$2KClO_3 = KClO_4 + KCl + O_2.$$

Upon warming the perchlorate with four parts sulphuric acid, perchloric acid distils over:—

$$2ClO_4K + H_2SO_4 = K_2SO_4 + 2HClO_4.$$

The pure acid is a mobile, colorless liquid, fuming strongly in the air; its specific gravity is 1.78 at 15°. It may be solidified by cold, melts about 15°, and boils at 110°. It cannot be preserved, since after a few days it decomposes with violent explosion. It also explodes in contact with phosphorus, paper, carbon, and other organic substances. It produces painful wounds when brought in contact with the skin. It dissolves in water with hissing, and with one molecule of the solvent forms the crystalline hydrate $HClO_4 + H_2O$, fusing at 50°; the crystals fume in the air and gradually deliquesce. The second hydrate—$HClO_4 + 2H_2O$—is a thick, oily liquid, resembling sulphuric acid, and boils unchanged at 208°. It may also be obtained by evaporating the aqueous solutions of perchloric and chloric acids. When the crystalline hydrate is distilled it breaks up into anhydrous perchloric acid and the second hydrate:—

$$2ClO_4H.H_2O = ClO_4H + ClO_4H.2H_2O.$$

Bromine yields the following oxygen compounds :—

$HBrO$	Hypobromous acid.
$HBrO_3$	Bromic acid.
$HBrO_4$	Perbromic acid.

The corresponding anhydrides are not known. The acids are perfectly analogous to the corresponding chlorine compounds.

Hypobromous Acid—$HBrO$—is formed when bromine water acts upon mercuric oxide; the aqueous solution can be distilled *in vacuo*, and possesses all the properties of hypochlorous acid.

Bromic Acid—BrO_3H. Bromates are formed by the action of bromine, in the heat, upon the aqueous solution of the alkalies or of barium hydroxide; an aqueous solution of the acid can be obtained from the barium salt by decomposing the latter with sulphuric acid. A more practical method of getting the free acid is to let bromine act upon silver bromate or oxidize bromine with hypochlorous acid :—

$$5Cl_2O + Br_2 + H_2O = 2BrO_3H + 10Cl.$$

The aqueous solution may be concentrated *in vacuo* until its content reaches 50.6 per cent. BrO_3H, and then closely corresponds to the formula $BrO_3H + 7H_2O$. When heated it breaks up into bromine, oxygen and water.

Perbromic Acid—BrO_4H—is said to be formed in the action of bromine vapor upon perchloric acid :—

$$ClO_4H + Br = BrO_4H + Cl.$$

and is perfectly similar to the latter.

Iodine forms the following anhydrides and acids :—

I_2O_5 HIO_3 — Iodic Acid.
(I_2O_7) HIO_4 — Periodic Acid.

Iodic Acid—HIO_3. Its salts (iodates) are formed in the same manner as those of chloric and bromic acids, by dissolving iodine in a hot solution of potassium or sodium hydroxide :—

$$6KOH + 3I_2 = 5KI + IKO_3 + 3H_2O.$$

The free acid can be obtained by the oxidation of iodine with strong nitric acid, or by means of chlorine; further, by the action of iodine upon chloric or bromic acids, whereby the iodine directly eliminates the chlorine and bromine :—

$$2HClO_3 + I_2 = 2HIO_3 + Cl_2.$$

Upon evaporating the aqueous solution the free iodic acid crystallizes in colorless rhombic tablets of specific gravity 4.63. The solution possesses strong oxidizing properties. When iodic acid is heated to 170° it decomposes into water and iodic anhydride :—

$$2HIO_3 = I_2O_5 + H_2O.$$

It is decomposed, similarly to chloric acid, by hydrochloric acid :—

$$2IO_3H + 10HCl = I_2 + 5Cl_2 + 6H_2O.$$

Reagents, like H_2S, SO_2 and HI, reduce it to iodine. Periodic acid sustains similar decompositions.

Iodic Anhydride—I_2O_5—is a white crystalline powder, which dissolves in water to form iodic acid. It decomposes at 300° into iodine and oxygen.

Periodic Acid—HIO_4—is produced by the action of iodine upon perchloric acid :—

$$2HClO_4 + I_2 = 2HIO_4 + Cl_2.$$

Upon the evaporation of the aqueous solution, the acid crystallizes out with two molecules of water (HIO_4, $2H_2O$—compare below). In the air, the crystals deliquesce, fuse at 130°, and at a higher temperature decompose into water and periodic anhydride, the latter at once breaking up into oxygen and iodic anhydride :—

$$2(HIO_4 + 2H_2O) = I_2O_5 + O_2 + 5H_2O.$$

The existence of the hydrates of periodic and perchloric acids, as well as of many others (see Sulphuric and Nitric acids), which we once regarded as molecular compounds (p. 175), is interpreted at present by the acceptance of hydroxyl groups, directly combined with the element of higher valence :—

$$ClO_4H + H_2O = \overset{VII}{Cl}O_2(OH)_3\text{— trihydrate or tryhydric acid.}$$
$$ClO_4H + 2H_2O = \overset{VII}{Cl}O\ (OH)_5\text{— pentahydrate or pentahydric acid.}$$
$$ClO_4H + 3H_2O = \overset{VII}{Cl}\ \ (OH)_7\text{— heptahydrate or heptahydric acid.}$$

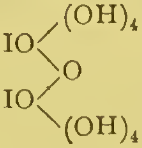
The extreme hydrates, $Cl(OH)_7$ and $I(OH)_7$, in which all seven affinities of the halogen atom are attached to hydroxyl groups, are not known, but probably exist in aqueous solution. As they give up water, and one atom of O becomes simultaneously united with two bonds to the halogen, they yield the lower hydrates—even to the monohydrate ClO_3OH. Perchloric acid continues monobasic in the polyhydrates, since but *one* hydrogen atom is replaced by metals :—

$$ClO_6H_5 + KOH = ClO_4K + 3H_2O.$$

On the other hand, periodic acid (IO_3OH) is not only monobasic, but as a pentahydrate ($IO(OH)_5$) can, like the polybasic acids, furnish also polymetallic salts as :—

$\overset{\text{VII}}{\text{IO}}\left\{\begin{matrix}(\text{OH})_3\\(\text{ONa})_2\end{matrix}\right.$ $\quad\overset{\text{VII}}{\text{IO}}\left\{\begin{matrix}(\text{OH})_2\\(\text{OAg})_3\end{matrix}\right.$ $\quad\overset{\text{VII}}{\text{IO}}(\text{O.Na})_5$ $\quad\overset{\text{VII}}{\text{IO}}(\text{OAg})_5.$

Salts also exist which are derived from condensed polyiodic acids, as:—


—Diperiodic acid, etc.

(Compare disulphuric, dichromic acid, etc.)

The existence of such salts plainly indicates that the hydrates of acids must be looked upon as hydroxyl compounds, and that iodine and the halogens are, in fact, heptads in their highest combinations.

The oxygen compounds of the halogens in some respects display a character exactly opposite to that of the hydrogen derivatives. While the affinity of the halogens for hydrogen diminishes with increasing atomic weight from Fl to I (see p. 66), the affinity for oxygen is the exact reverse. Fluorine is not capable of combining with oxygen; the chlorine and bromine compounds are very unstable, and are generally not known in free condition; the iodine derivatives, on the contrary, are the most stable. In accord with this is the fact that in the higher oxygen compounds chlorine and bromine are set free by iodine, while in the hydrogen and metallic compounds of the halogens the direct reverse is the case, viz., that iodine and bromine are replaced by chlorine.

Further, the oxygen compounds exhibit the remarkable peculiarity that their stability increases with the addition of oxygen. The lowest acids, $HClO$, $HBrO$, $HClO_2$, are very unstable, even in their salts; they possess a very slight acid character, and are, too, separated from their salts by carbon dioxide. The most energetic and most stable are the highest acids, $HClO_4$, $HBrO_3$, HIO_3, in which the higher valence of the halogens appears. In the sulphur and nitrogen groups those oxides, in which the elements manifest their maximum valence, are the most stable (compare p. 174).

The peculiar behavior of the oxygen compounds of the halogens, their variable stability and decomposition, and their modes of formation, find a clearer explanation in their thermo-chemical relations. All oxide compounds of chlorine and bromine are endothermic, *i. e.*, heat is rendered latent in their production from the elements (compare p. 67). They do not result, therefore, by direct union of the elements; further, they are not very stable, decompose readily with elimination of oxygen, and then oxidize strongly. The heat, appearing in the formation of chlorine monoxide, and of the hypothetical pentoxides, Cl_2O_5 and Br_2O_5 (in their production from the elements and solution in water), corresponds to the symbols:—

$$(Cl_2,O - \text{gas}) = -18.0;\ (Cl_2,O_5,Aq.) = -20.4\ (Br_2,O_5,Aq.) = -43.5.$$

In the formation of iodine pentoxide and iodic acid heat is liberated :—

$$(I_2,O_5) = +44.8;\ (I,O_3,H) = +57.8.$$

This explains its stability in comparison with the chlorine and bromine compounds, and also the direct production of iodic acid by the oxidation of iodine. When the pentoxides are compared with each other, it is seen that the most heat is rendered latent in the formation of bromine pentoxide, Br_2O_5—the affinity of bromine for oxygen, consequently, is the lowest, that of iodine the greatest. This is also evident from the heat of formation of the acids, in dilute aqueous solution, or of the potassium salts in solid condition :—

$$(Cl,O_3,H,Aq.) = 23.9;\ (Br,O_3,H,Aq.) = 12.4;\ (I,O_3.H,Aq.) = 55.7;$$
$$(Cl,O_3,K) = 94.6;\ (Br,O_3,K) = 87.6;\ (I,O_3,K) = 128.4.$$

We now understand why chlorine and bromine are separated from chloric and bromic acids by iodine, with formation of iodic acid, while bromine does not act upon chloric acid. Later, we will observe that also in the groups of oxygen, nitrogen and carbon, the second members (sulphur, phosphorus and silicon) exhibit a greater heat-disengagement in their oxygen derivatives, than the immediately succeeding members (selenium, arsenic); the former belong to the second, and the latter to the third period of the natural system of the elements.

OXYGEN COMPOUNDS OF THE ELEMENTS OF THE SULPHUR GROUP.

The elements sulphur, selenium, and tellurium combine with two atoms of H, and also yield oxygen acids, which contain 2 H atoms :—

$$H_2S \qquad (SO_2H_2) \qquad H_2SO_3 \qquad H_2SO_4.$$

In these acids 1 and 2 atoms of H can be replaced by metals ; hence they are *dibasic*. By the replacement of 1 atom of H we get the so-called *acid* or *primary salts*, while the *neutral* or *secondary salts* are obtained by the replacement of both hydrogen atoms :—

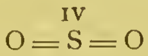
SO_4KH	SO_4K_2.
Acid potassium sulphate.	Neutral potassium sulphate.

1. OXYGEN COMPOUNDS OF SULPHUR.

......	(SO_2H_2) Hyposulphurous acid.
SO_2 Sulphurous anhydride.	SO_3H_2 Sulphurous acid.
SO_3 Sulphuric anhydride.	SO_4H_2 Sulphuric acid.

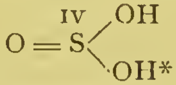
In addition to these compounds there are others of more complicated nature. They will be studied later.

The structure of the former may be expressed by the following formulas:—

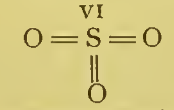


$$O = \overset{\text{IV}}{S} = O$$

Sulphur dioxide.

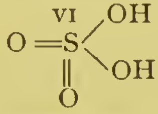


Sulphurous acid.



$$O = \overset{\text{VI}}{\underset{\underset{O}{\|}}{S}} = O$$

Sulphur trioxide.



Sulphuric acid.

Sulphur Dioxide, SO_2, or sulphurous anhydride, is formed by burning sulphur or sulphides in the air: $S + \underset{\text{1 vol.}}{O_2} = \underset{\text{1 vol.}}{SO_2}$.

The combustion may also be effected by the action of metallic oxides (copper oxide, manganese peroxide) which give up their oxygen quite readily. It is most conveniently prepared for laboratories by heating sulphuric acid with mercury or copper:—

$$2H_2SO_4 + Cu = \underset{\substack{\text{Copper} \\ \text{sulphate.}}}{CuSO_4} + SO_2 + 2H_2O.$$

The acid is similarly decomposed by heating it with carbon:—

$$2SO_4H_2 + C = 2SO_2 + CO_2 + 2H_2O.$$

By this method we get a mixture of carbon and sulphur dioxides, which are separated with difficulty. A more convenient method for preparing sulphur dioxide consists in allowing ordinary English sulphuric acid to act upon calcium sulphite, $CaSO_3$. The latter is

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* The structure of sulphurous acid must probably be expressed by the formula, $H - \overset{\text{IV}}{S}O_2 - OH$, according to which 1 atom of H is connected with sulphur, but the other is contained as hydroxyl. This appears from the carbon derivatives of sulphurous acid. Probably both structural cases exist in compounds as two isomeric series of neutral ethers of the acid are known.

mixed with burnt gypsum (⅓ part) and water, then moulded into cubes, which can be introduced into a Kipp's generator, as in the preparation of oxygen (p. 81). Owing to its solubility in water, sulphur dioxide must be collected over mercury.

Sulphur dioxide is a colorless gas, with a suffocating odor. Its density is 32.03 ($H = 1$), corresponding to the molecular formula $SO_2 = 64.06$. It condenses at —15°, or at ordinary temperatures under a pressure of two atmospheres, to a colorless liquid, of specific gravity 1.45, which crystallizes at —76° and boils at —10°. Upon evaporation the liquid sulphur dioxide absorbs much heat; so that if some of the liquid is poured upon mercury in a clay crucible, and the evaporation accelerated by blowing air upon it, the metal will solidify. Water dissolves 50 volumes of sulphur dioxide gas with liberation of heat. The gas is again set free upon application of heat. The solution shows all the chemical properties of the free gas.

Sulphur dioxide has great affinity for oxygen. The gases combine when dry; if their mixture be conducted over feebly heated platinum sponge* sulphur trioxide results:—

$$\underset{\text{2 vols.}}{2SO_2} + \underset{\text{1 vol.}}{O_2} = 2SO_3.$$

In aqueous solution the dioxide slowly absorbs O from the air, and becomes sulphuric acid:—

$$SO_2 + H_2O + O = H_2SO_4.$$

Aqueous sulphur dioxide is converted more rapidly into sulphuric acid by the action of Cl, Br, and I:—

$$SO_3H_2 + H_2O + Cl_2 = SO_4H_2 + 2HCl.$$

Here the decomposition of a molecule of water is effected in consequence of the affinity of the halogen for hydrogen and of sulphurous acid for oxygen. On adding sulphurous acid to a dark-colored iodine solution the latter is decolorized.

Similarly, sulphurous anhydride and its solution withdraw oxygen from many compounds rich in that element; hence it deoxidizes strongly and passes over into sulphuric acid. Thus chromic acid is reduced to oxide, and the red solution of permanganic acid is decolorized with formation of manganous salts. Many organic coloring substances, like those of flowers, are decolorized by it. This prop-

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* Instead of platinum sponge, platinized asbestos may be applied; this is obtained by immersing asbestos in a platinic chloride solution, then in ammonium chloride, and afterward drying and igniting.

erty is what leads to its application in the bleaching of wools and silks, which are strongly attacked by the ordinary chlorine bleaching agents (p. 52).

The dioxide may be deoxidized by strong reducing agents; thus sulphur is separated out by H_2S :—

$$SO_2 + 2H_2S = 2H_2O + 3S.$$

If, however, both gases are strongly diluted by other neutral gases, the action is but very slow.

A mixture of equal volumes of SO_2 and Cl_2 unites in direct sunlight to thionyl chloride, SO_2Cl_2. (p. 200). When sulphur dioxide acts upon warmed phosphoric chloride, the products are phosphorus oxychloride, and the compound $SOCl_2$:—

$$SO_2 + PCl_5 = POCl_3 + SOCl_2.$$

Chlorthionyl—$SOCl_2$—may be viewed as sulphur dioxide in which one atom of O is replaced by two atoms of chlorine. It is a colorless liquid with a sharp odor, and boils at 78°. Water decomposes it into hydrogen chloride and sulphurous acid :—

$$SOCl_2 + H_2O = SO_2 + 2HCl.$$

Sulphurous Acid—H_2SO_3—is not known in free condition, but is probably present in the aqueous solution of SO_2. On cooling the concentrated solution to 0°, colorless cubical crystals separate, which have the composition $(SO_2 + 15H_2O)$ or $(SO_3H_2 + 14H_2O)$. If the aqueous solution is allowed to stand for some time, especially in sunlight, sulphur separates with formation of sulphuric acid :—

$$3SO_2 + 2H_2O = 2SO_4H_2 + S.$$

Sulphurous acid is dibasic and forms two series of salts; the primary ($KHSO_3$) and secondary (K_2SO_3).

Sulphites.—These are obtained by saturating solutions of bases with SO_2. When sulphurous acid is separated out from its salts by stronger acids it decomposes into its anhydride and water :—

$$Na_2SO_3 + 2HCl = 2NaCl + SO_2 + H_2O.$$

Thermo-chemical Deportment.—Sulphur dioxide is a very powerful exothermic compound. 71.0 Cal., are set free in its formation from sulphur (solid) and oxygen. When it dissolves in much water there is an additional disengagement of 7.7 Cal., so that the heat of formation of the hypothetical sulphurous acid in dilute aqueous solution (from sulphur, oxygen and water) equals 78.7 calories :—

$$(S,O_2) \text{ gas} = 71.0;\ (SO_2,Aq.) = 7.7;\ (S,O_2,Aq.) = 78.7.$$

In consequence of this great loss of energy the dioxide is a very stable compound; it is only at high temperatures that it sustains a partial separation into sulphur and oxygen. Its whole chemical deportment fully corresponds to its thermo-chemical relations, *e. g.*, its reduction by hydrogen sulphide:—

$$\underset{(71.0)}{SO_2} + \underset{(2 \times 4.5)}{H_2S} = S_2 + \underset{(2 \times 58.0)}{2H_2O \text{ vapor}} \ldots (+36.0 \text{ Cal.})$$

For its behavior toward oxygen, see p. 189.

Hydrosulphurous Acid.—H_2SO_2 or $S_2O_4H_2$. On adding zinc to the aqueous solution of sulphurous acid the metal dissolves without liberation of hydrogen. A yellow solution is obtained, which decolorizes indigo and litmus solutions energetically. These properties are due to the hydrosulphurous acid contained in the solution, formed there by the action of the H set free by the zinc upon a second molecule of SO_3H_2:—

$$H_2SO_3 + Zn = SO_3Zn + H_2, \text{ and}$$
$$H_2SO_3 + H_2 = SO_2H_2 + H_2O.$$

The pure aqueous solution of the acid is obtained by the decomposition of its salts. Its solution has an orange yellow color, reduces powerfully, bleaches and soon decomposes with separation of sulphur. The bleaching action of this lowest oxygen compound of sulphur reminds us of a similar behavior of the lower oxygen derivatives of chlorine and bromine.

The salts are more stable than the acid. The sodium salt is obtained by the action of zinc filings upon a concentrated solution of primary sodium sulphite. Its composition is not established with certainty; it corresponds to either the formula SO_2 HNa or $S_2O_4Na_2$. The salt solutions absorb oxygen very rapidly from the air and change to sulphites.

Two peculiar oxides of sulphur, resembling peroxides, are sulphur sesquioxide and sulphur heptoxide.

Sulphur Sesquioxide—S_2O_3—is obtained by the solution of flowers of sulphur in anhydrous sulphuric anhydride; it separates out in blue drops, which solidify to a mass resembling malachite. It decomposes gradually, more rapidly on warming, into SO_2 and sulphur. It is very violently broken up by water, with formation of sulphur, SO_2,SO_4H_2 and polythionic acids. It dissolves with a blue color in concentrated sulphuric acid.

Sulphur Heptoxide—S_2O_7—is produced by the action of a silent electric discharge of great tension upon a mixture of SO_2 or SO_3 and oxygen. It separates, in oily drops, which solidify to a crystalline mass at 0°. Upon standing, but especially upon warming, it gradually decomposes into SO_3 and oxygen:—

$$S_2O_7 = 2SO_3 + O.$$

It fumes strongly in the air, and with water decomposes into sulphuric acid and oxygen:—

$$S_2O_7 + 2H_2O = 2SO_4H_2 + O.$$

The solution of sulphur heptoxide in sulphuric acid is formed by the electrolysis of the latter acid diluted with water (40 per cent. H_2SO_4). It appears at the anode together with oxygen and ozone (p. 94). The solution is also produced on the addition of aqueous hydrogen peroxide to strongly cooled and concentrated sulphuric acid; active oxygen is evolved simultaneously.

The solution of the heptoxide in sulphuric acid shows oxidation reactions similar to those of hydrogen peroxide (p. 104). It oxidizes ferrous sulphate to ferric oxide, gradually separates iodine from potassium iodide, and decolorizes the blue solution of indigo-sulphuric acid. It cannot, however, decolorize a potassium permanganate solution, does not impart a blue coloration to a chromic acid solution, nor does it act upon a titanic acid solution, and thus may be distinguished from hydrogen peroxide (p. 104).

If the aqueous sulphuric acid should contain more than 60 per cent. H_2SO_4 when electrolyzed, hydrogen peroxide will also result from the decomposition of the heptoxide first produced (p. 102). It is also formed by the gradual decomposition of sulphuric acid containing the heptoxide, S_2O_7, on standing. This will occur rapidly if the acid be concentrated beyond 70 per cent. by the addition of more acid.

Persulphates.—By the electrolysis of potassium hydrogen sulphate in a divided cell, Marshall obtained potassium persulphate—KSO_4. This salt forms tabular, apparently asymmetric crystals. It leaves secondary potassium sulphate on ignition, oxygen and sulphur trioxide being evolved. It is slightly decomposed by hot water. At the ordinary temperature its conversion into acid potassium sulphate with liberation of oxygen is slow. The pure aqueous solution of the salt is neutral to test paper. It readily oxidizes ferrous sulphate to ferric sulphate. It does not react immediately with potassium iodide; heat hastens the reaction. It bleaches litmus and turmeric slowly. It rapidly oxidizes a warm solution of potassium ferrocyanide to potassium ferricyanide. Alcohol is oxidized to aldehyde by it. Strong nitric acid and sulphuric acid evolve oxygen as ozone from solid persulphates on the application of a gentle heat. Hydrochloric acid liberates chlorine. Ammonium persulphate—NH_4SO_4—has also been prepared. Its reactions are similar to those of the potassium salt. It is utilized in the preparation of other persulphates.

The formation of pure persulphates in solid crystalline form conclusively demonstrates that persulphuric anhydride and persulphuric acid are not peroxides (*Jr. Ch. Soc.*, 60, 771).

Sulphur Trioxide—SO_3—or sulphuric anhydride, is produced, as previously described, by the union of SO_2 and oxygen, aided by platinum black; or when SO_2 and air are conducted over ignited oxide of iron (Wöhler). It can also be made by heating sodium or potassium pyrosulphate (p. 198). It is most conveniently obtained by heating fuming (Nordhausen) sulphuric acid (p. 198); the escaping white fumes are condensed in a chilled receiver. Sulphur trioxide exists in two different (polymeric) modifications. In the one form obtained by cooling the vapors, there is produced a white, asbestos-like mass which, after fusion, crystallizes in long, colorless prisms; it melts at 16° and boils at about 46°. The vapor density agrees with the formula SO_3. By keeping it below 25° it passes into another so-called solid modification, which does not fuse until above 50°, and then reverts to the liquid variety.

According to later investigations of Weber neither modification is the pure anhydride, as both contain water. He obtained the pure anhydride by subjecting the asbestos-like variety to repeated and careful distillations in a closed tube. It is a readily mobile liquid, of specific gravity 1.940 at 16°, but solidifies to long, transparent, needles, resembling saltpetre. The crystals fuse at 14.8° and boil at 46.2°. By the addition of a small quantity of moisture the transparent crystals pass into the asbestos-like needles of the ordinary anhydride.

Sulphuric oxide fumes strongly in the air, and attracts moisture with avidity. When thrown on water it dissolves with hissing, to form sulphuric acid ($SO_3 + H_2O = H_2SO_4$).

When the vapors are led through heated tubes they are decomposed into SO_2 and oxygen.

Thermo-chemical Deportment.—When sulphur dioxide and oxygen combine to form liquid sulphur trioxide 32.1 Cal., are disengaged, so that its heat of formation from the elements is 103.2 Cal. :—

$$(SO_2,O) \text{ liquid} = 32.1. \quad (S,O_3) \text{ liquid} = 103.2.$$

inasmuch as the heat of formation of the dioxide = 71.0 Cal. Generally, when the formation of several compounds is possible in a reaction, that one is produced which sets free the most heat. Thus carbon yields CO_2 and not CO. But when sulphur burns it yields SO_2 almost exclusively and not SO_3. This is due to the instability of the trioxide, which at a red heat decomposes at once into SO_2 and O.

It is further necessary to bear in mind that in the formation of the more complex compounds, a great number of atoms or molecules are acting simultaneously, and therefore, at least in the coöperation of gases, the simpler compounds can be more readily produced. We now comprehend why reactions such as $S_2 + 3O_2 = 2SO_3$, $N_2 + 3H_2 = 2NH_3$ and $C_2 + 4H_2 = 2CH_4$, do not usually take place. And another consideration is that all bodies having a high heat of formation and decomposed at a high heat, must have their heat of formation removed or conducted away, in order that their production may be at all possible. This behavior explains many phenomena which apparently contradict the thermo-chemical principles, as for example, reactions generating little heat, taking place more readily than those having a greater heat-disengagement. The catalytic action of many metals, *e.g.*, platinum, in the reaction, $SO_2 + O = SO_3$, is very likely due to their conducting off the heat.

Another case is the greater reactivity of many bodies where they form a galvanic chain, because in this way the chemical energy is removed, as electricity, *e.g.*, the union of hydrogen and oxygen at ordinary temperatures due to the formation of a polarization current.

On dissolving sulphur trioxide in much water to form aqueous sulphuric acid, 39.1 Cal. are disengaged. The production, therefore, of the aqueous acid from sulphur, oxygen, and water equals (including the heat of formation of SO_3) 142.4 Cal. :—

$$(SO_3, Aq.) = 39.1; \quad (S, O_3, Aq.) = 142.4.$$

If we add to this the heat of formation of water (liquid)—68.3 Cal.,—the heat of formation of sulphuric acid ($H_2SO_4 = SO_3 + H_2O$) from the elements in dilute aqueous solution will be:—

$$(S, O_4, H_2, Aq.) = 210.7.$$

The heat of solution of anhydrous sulphuric acid, in much water, equals 17.8 Cal.; hence the heat of formation of anhydrous sulphuric acid from its elements is:—

$$210.7 - 17.8 = 192.9:$$

$$(SO_4H_2, Aq.) = 17.8. \quad (S, O_4, H_2) = 192.9.$$

For the relations of selenic and telluric acids, see p. 204.

SULPHURIC ACID—H_2SO_4.

This acid has long been known and is extensively applied in technology, etc. Besides the reactions already mentioned, it arises in the oxidation of sulphur by nitric acid. It was obtained formerly by heating ferrous sulphate ($FeSO_4$); at present, however, it is almost exclusively manufactured in large quantities, after the so-called English lead chamber process. This method is based upon the conversion of SO_2 into SO_4H_2. Sulphur or pyrite (FeS_2), is roasted in ovens, and the disengaged SO_2 immediately conducted, together with air, into a series of large leaden chambers in which it is frequently brought in contact with nitric acid and steam. By the combined action of these substances (sulphur dioxide, nitric acid, oxygen of the air and water) sulphuric acid is formed in the chambers and collects upon the floor of the same.

The lead chamber process is very complicated, being influenced by the quantity of the reacting substances and the temperature, and as yet is not fully explained. It is most simply represented as follows: in the presence of water, the nitric acid oxidizes the SO_2 to sulphuric acid, and the former is reduced to nitric oxide or nitrogen dioxide:—

$$3SO_2 + 2HNO_3 + 2H_2O = 3H_2SO_4 + 2NO.$$

The oxygen of the air (which entered the chambers simultaneously with the SO_2) and the steam convert the NO again into nitric acid:—

$$2NO + 3O + H_2O = 2HNO_3,$$

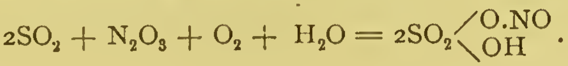
and this converts a fresh portion of SO_2 into sulphuric acid. Or, the nitric oxide forms N_2O_3 and NO_2 by union with oxygen, and these in the presence of steam oxidize sulphur dioxide to sulphuric acid:—

$$SO_2 + H_2O + N_2O_3 = SO_4H_2 + 2NO$$

and

$$SO_2 + H_2O + NO_2 = SO_4H_2 + NO.$$

The regenerated nitric oxide is again subjected to the same transformations. The chamber gases, according to the latest investigations of Lunge and Naeff, contain only nitrogen trioxide of the oxides of nitrogen, and in Lunge's opinion the lead chamber process depends chiefly upon the intermediate formation of nitrosylsulphuric acid. At first nitrogen trioxide, sulphur dioxide, oxygen, and a little water react upon each other, and the product is free, solid nitrosylsulphuric (p. 211):—



$$2SO_2 + N_2O_3 + O_2 + H_2O = 2SO_2\begin{cases} O.NO \\ OH \end{cases}.$$

The excess of water in the lead chamber immediately converts this product into sulphuric acid and nitrogen trioxide:—

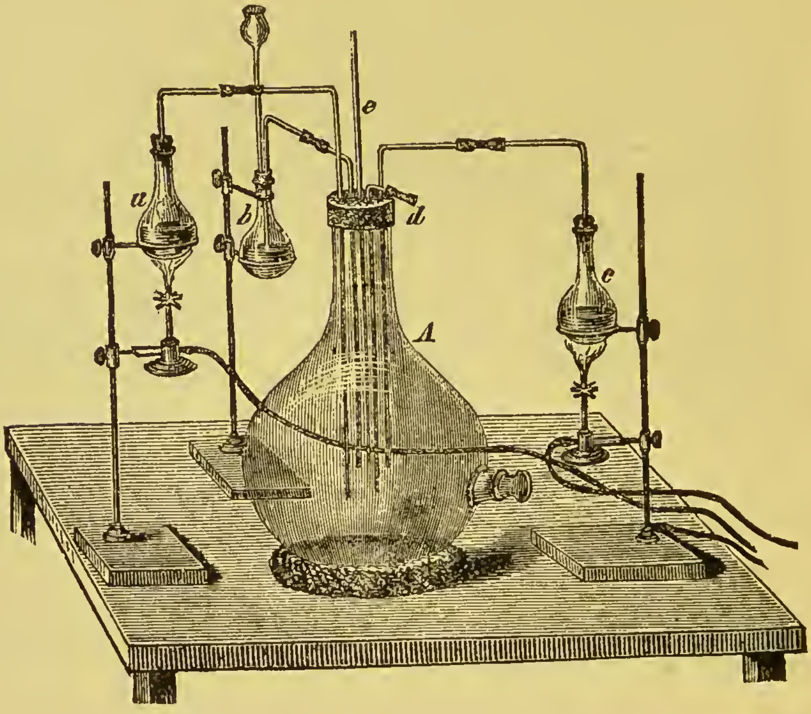
$$2SO_2\left\langle\begin{matrix}O.NO\\OH\end{matrix}\right. + H_2O = 2SO_2\left\langle\begin{matrix}OH\\OH\end{matrix}\right. + N_2O_3.$$

The trioxide, regenerated in this manner, acts again upon new portions of the sulphur dioxide. According to Lunge, nitrosylsulphuric acid is formed upon the very first action of the nitric acid introduced into the lead chamber:—

$$SO_2 + NO_2.OH = SO_2\left\langle\begin{matrix}O.NO\\OH\end{matrix}\right.$$

and it then reacts in the manner already indicated. In this way, apparently, one and the same quantity of nitric acid, by sufficient oxygen access and water, changes an unlimited amount of SO_2 into sulphuric acid; the oxides of nitrogen act, as it were, as carriers of oxygen. As much as 2–3 per cent. of nitric acid is lost in practice. This is probably due to the further reduction of the nitrogen oxides to nitrous oxide (N_2O) and nitrogen (which are not absorbed in the Gay-Lussac towers). The recent studies of Raschig point to the intermediate formation of amidosulphonic acids in the lead chamber process, and the loss in nitrogen is due to their conversion into ammonia.

FIG. 84.



In practice, the active nitrogen oxides (N_2O_3 and NO_2) are carried along and withdrawn from the action by means of the escaping nitrogen and excess of air. To avoid any further loss of nitric acid by this means, the escaping brown gases are conducted through the so-called Gay-Lussac tower. This is constructed from lead sheets, and filled with pieces of coke, over which concentrated sulphuric acid constantly trickles. The acid completely absorbs the nitrogen oxides N_2O_3, NO_2 and NO, with formation of nitrosylsulphuric acid (see p. 211). The nitrogen oxides can be regained from the acid—the so-called nitroso-acids—collected at the bottom of the tower, and made useful in the production of sulphuric acid in the chambers. This is effected at present, in the so-called *Glover tower*, which is constructed of lead plates and fire-proof bricks, and inserted between the sulphur ovens and lead chambers. In this the nitroso-acid (diluted with the previously obtained chamber acid) is allowed to run over fire-brick, while the hot gases of combustion from the sulphur ovens stream against it. This cools the hot gases to the required temperature (70–80°), water evaporates from the chamber acid, and, at the same time, the nitrogen oxides are set free (see p. 212), and carried into the lead chambers. Hence, the Glover tower serves, not only for complete utilization of the nitrogen oxides, but also for the concentration of the chamber acid.

The chamber process may be illustrated by the following laboratory experiment: A large, glass flask (Fig. 84) *A* replaces the lead chamber; in its neck are introduced, by means of a cork, several glass tubes, which serve to introduce the various gases. In *a*, SO_2 is developed by heating a mixture of H_2SO_4 and Hg or copper strips. The flask *b* contains some dilute nitric acid and copper turnings, from which NO is evolved. Water is boiled in *c* to afford steam. Air enters through *d* while the excess of gases escapes through *e*. By the meeting of NO with the air, red fumes of nitrogen dioxide (NO_2) and nitrogen trioxide (N_2O_3) arise, and these in presence of water change the sulphur dioxide to sulphuric acid (p. 193).

The regenerated nitric oxide yields NO_2 with the oxygen of the air, and converts another portion of SO_2 into sulphuric acid. In time aqueous sulphuric acid collects upon the bottom of the vessel. If, at first, only SO_2, NO and air enter without the steam, we get (by aid of the moisture of the air) the compound $SO_2\left\{\begin{matrix}NO_2\\OH\end{matrix}\right.$ (the so-called nitrosulphonic acid) which covers the walls of the vessel with a white crystalline sublimate (comp. p. 212). These crystals, known as lead-chamber crystals, are also formed in the technical manufacture of sulphuric acid, when an insufficient quantity of steam is conducted into the chambers. Water decomposes them into sulphuric acid and nitrogen oxides.

The acid collecting in the chambers (chamber acid) possesses, when the operation has been properly conducted, the specific gravity 1.5 (50° according to Beaumè); it contains about 60 per cent. H_2SO_4 and 40 per cent. H_2O. For concentration the chamber acid is first heated in open pans until the specific gravity reaches 1.72 (60° Beaumè). The lead vats are strongly attacked by further evaporation, hence the acid is finally heated in glass vessels, or, better, platinum retorts, until the residual liquid has acquired the specific gravity, 1.83 (65.5° Beaumè). It is now entered upon trade under the name *crude sulphuric acid* (*Acidum sulphuricum crudum*). It still contains about 8 per cent. water and traces of lead and arsenic. By further concentration we can obtain 95–96 per cent. H_2SO_4 (extra concentrated acid).

By the distillation of the crude English acid an aqueous solution at first distils over (⅓ distillate), but at 330° we obtain almost pure

H_2SO_4 (*Acidum sulphuricum* or *destillatum*). This has the specific gravity 1.854 at 0° or 1.842 at 12°, and contains about 1.5 per cent. water. On cooling this to —35° white crystals separate, which, after repeated recrystallization fuse at + 10.5°; this is the *anhydrous* acid, H_2SO_4. The crystalline acid is more readily obtained by cooling the 96–98 per cent. sulphuric acid to 0° or — 10°, and then adding already-formed crystals. This is the manner in which the anhydrous acid is produced technically; the crystals are separated from the liquid, hydrous acid by a centrifugal machine.

Pure anhydrous sulphuric acid, H_2SO_4, has the specific gravity 1.8372 at 15°, and is, therefore, lighter than slightly hydrous acid. When this is heated, white fumes of SO_3 escape at 40°; the liquid begins to boil at 200°, and at 330° the acid, with 1.5 per cent. H_2O, again distils over.

From these data it is obvious that sulphuric acid, even at a gentle heat, sustains a partial decomposition (dissociation) into SO_3 and H_2O, which again unite to form sulphuric acid when they cool. The vapor density, corresponding to the molecular formula $H_2SO_4 = 98$, must be equal to 49 ($\frac{98}{2}$). The vapor density of sulphuric acid has been found to be 36.0 (or 2.5-air = 1) at 332° (near its boiling point). It diminishes at higher temperatures, and is 24.5 at 416°, where it is constant. This behavior is explained by the dissociation of the acid molecules, according to the equation:—

$$\underset{1\text{ vol.}}{SO_4H_2} = \underset{1\text{ vol.}}{SO_3} + \underset{1\text{ vol.}}{H_2O}.$$

The vapor density corresponding to the molecular formula $H_2SO_4 = 98$ must be $\frac{98}{2} = 49$; that of the mixture of the decomposition products, filling a volume twice as large, is $\frac{49}{2} = 24.5$. Hence, the dissociation of the acid is complete at 416°, while it is only about 34 per cent. at 332° (p. 96).

Concentrated sulphuric acid is a thick, oily liquid. On cooling, a sulphuric acid containing about 15 per cent. water to 0°, large six-sided prisms of the hydrate $SO_4H_2 + H_2O$ separate; these fuse at + 8.5°, and give up water at 250°. The *second hydrate*, $SO_4H_2 + 2H_2O$, corresponding to the maximum contraction, has the specific gravity 1.63, and yields water at 195°. The concentrated acid possesses an extremely great affinity for water, and absorbs aqueous vapor energetically, hence is applied in the drying of gases and in desiccators. It unites with water with the evolution of considerable heat, and, for this reason, it is practically recommended, in mixing the acid, to pour the latter in a thin stream into the water, and not the reverse, as otherwise explosive phenomena occur. In mixing sulphuric acid with water, a contraction of the mixture takes place; its maximum corresponds to the hydrate $SO_4H_2 + 2H_2O$.

The existence of the hydrates of sulphuric acid is explained, as in the case of periodic acid, by the supposition of hydroxyl groups:—

$SO_4H_2 + 2H_2O = S(OH)_6$ Hexahydroxyl sulphuric acid.
$SO_4H_2 + H_2O = SO(OH)_4$ Tetra " " "
$SO_4H_2 = SO_2(OH)_2$ Normal sulphuric acid.

The tetra- as well as the hexahydroxylsulphuric acid yield only salts of the normal dibasic acid, when they are acted upon by bases. Salts, in which several H atoms are replaced by metals, are not known.

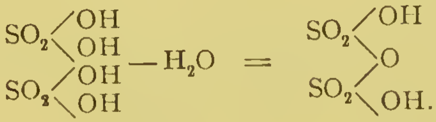
The affinity of sulphuric acid for water is so great that the former withdraws the hydrogen and oxygen from many substances, with the production of water. In addition to carbon, many organic compounds contain hydrogen and oxygen in the proportion in which these elements yield water. The withdrawal of H and O from such substances leaves the carbon. This explains the charring action of H_2SO_4 upon wood, sugar, and paper. When sulphuric acid acts upon alcohol (C_2H_6O), ethylene, C_2H_4 (p. 155), results.

By conducting H_2SO_4 over red hot porous bodies, it is decomposed into sulphur dioxide, water, and oxygen :—

$$H_2SO_4 = SO_2 + H_2O + O.$$

This decomposition affords us a method for manufacturing oxygen technically ; the sulphur dioxide is absorbed by water and afterward converted into H_2SO_4. When heated with S, P, C, and some metals (Hg, Cu), the acid is reduced to dioxide (p. 187). Nearly all the metals are dissolved by it, forming salts ; only lead, platinum, and a few others are scarcely attacked at all. It is a very strong acid, and, when heated, expels most other acids from their salts; upon this depends its application in the manufacture of hydrochloric and nitric acids. The barium salt ($BaSO_4$) is characterized by its insolubility in water and acids; therefore, sulphuric acid added to solutions of barium compounds produces a white pulverulent precipitate, which serves to detect small quantities of the acid.

Pyrosulphuric, or Disulphuric Acid—$H_2S_2O_7$.—On withdrawing one molecule of water from two molecules of the acid there results the compound $S_2O_7H_2$, whose formation and structure may be represented by the following formula :—



$$\begin{matrix} SO_2 \begin{cases} OH \\ OH \end{cases} \\ SO_2 \begin{cases} OH \\ OH \end{cases} \end{matrix} - H_2O = \begin{matrix} SO_2 \langle OH \\ \quad > O \\ SO_2 \langle OH. \end{matrix}$$

As this contains two hydroxyl groups it is a dibasic acid ; yet its manner of formation shows that it possesses an *anhydride* character. Later, we will observe that almost all polybasic acids, like phosphoric acid, $PO(OH)_3$, silicic acid, $SiO(OH)_2$, and chromic acid, CrO_2

$(OH)_2$, are capable, by the condensation and the elimination of several molecules of water, of forming like derivatives, which bear the name *Poly-* or *Pyro-acids.*

The disulphuric acid is contained in the so-called *fuming* or *Nordhausen sulphuric acid* (*Acidum sulphuricum fumans*), which is obtained by heating dehydrated ferrous sulphate—green vitriol ($FeSO_4$). It is a thick, oily, strongly-fuming liquid, of specific gravity 1.85–1.9. When it is cooled, large colorless crystals of $H_2S_2O_7$ separate; these fuse at 35°. Heat breaks it up into sulphuric acid and sulphur trioxide, which volatilizes:—

$$S_2O_7H_2 = SO_4H_2 + SO_3.$$

Conversely, disulphuric acid may be obtained by dissolving SO_3 in sulphuric acid:—$SO_4H_2 + SO_3 = S_2O_7H_2$. The production of fuming sulphuric acid also depends on this, as it may be regarded as a solution of SO_3 (or $S_2O_7H_2$) in excess of sulphuric acid.

Technically, fuming sulphuric acid is obtained from pyrites (FeS_2)—(at present only in Bohemia). The decomposition of the pyrites in the air affords ferrous sulphate and ferric oxide. The first can be dissolved out with water. The solution is evaporated, and the residue roasted in a reverberatory furnace, whereby the ferrous salt is changed to ferric salts. The latter are then distilled from earthen retorts, when sulphuric acid and the trioxide pass over and are collected in the receivers:—

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3.$$

$$Fe_2\left\{\begin{matrix}(SO_4)_2\\(OH)_2\end{matrix}\right. = Fe_2O_3 + SO_3 + SO_4H_2.$$

The residue, consisting of red ferric oxide, finds application as colcothar (*caput mortuum*) in polishing and as a paint.

Solid, crystalline pyrosulphuric acid has been recently introduced into the market as a substitute for the fuming liquid sulphuric acid. It is made by conducting the theoretical amount of sulphur trioxide into concentrated sulphuric acid (see above). Sulphur trioxide is prepared by two distinct methods at present.

In Winkler's method sulphuric acid of 66° Baumé is first allowed to run into retorts raised to a red heat. The mixed gases, SO_2, O and H_2O (p. 195) resulting from this action, are freed from steam by passing through a coke tower through which there trickles conc. sulphuric acid. The dry mixture is then conducted over ignited platinized asbestos (p. 188) and the resulting SO_3 collected in concentrated sulphuric acid.

The more recent method of Wolter consists in producing sodium pyrosulphate by heating sodium sulphate with concentrated sulphuric acid:—

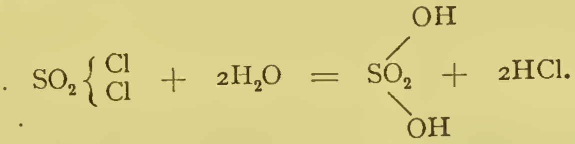
$$\underset{\text{Sodium sulphate.}}{SO_4Na_2} + SO_4H_2 = \underset{\text{Sodium pyrosulphate.}}{S_2O_7Na_2} + H_2O.$$

An intermediate product in this reaction is primary sodium sulphate—SO_4NaH. Upon stronger heating sod. pyrosulphate is broken up into the neutral sulphate and sulphur trioxide:—

$$S_2O_7Na_2 = SO_4Na_2 + SO_3.$$

The sulphur trioxide which escapes is collected in sulphuric acid, and the residual sodium sulphate again converted into pyrosulphate.

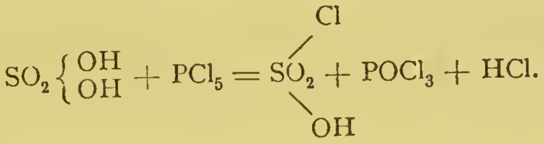
Sulphuric Acid Chlor-anhydrides.—Under the name of halogen anhydrides we understand the derivatives resulting from the replacement of OH in hydroxides by halogens. Conversely, the chlor-anhydrides, by the action of water, pass into the corresponding acids:—



$$SO_2\begin{cases}Cl\\Cl\end{cases} + 2H_2O = SO_2\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix} + 2HCl.$$

The ordinary method for the preparation of the chlor-anhydrides consists in permitting PCl_5 to act on the acids. Sulphuric acid has two hydroxyl groups; therefore it can furnish two chlor-anhydrides. The

first, $SO_2\begin{matrix}\diagup Cl\\ \diagdown OH\end{matrix}$ — *Sulphuryl Hydroxy-chloride* or *Chlorsulphonic Acid*—results when 1 molecule of PCl_5 acts upon 1 molecule of H_2SO_4:—



$$SO_2\begin{cases}OH\\OH\end{cases} + PCl_5 = SO_2\begin{matrix}\diagup Cl\\ \diagdown OH\end{matrix} + POCl_3 + HCl.$$

The resulting $POCl_3$ acts upon two additional molecules of SO_4H_2, with formation of metaphosphoric, hydrochloric, and chlorsulphonic acids.

It is formed, too, by the direct union of SO_3 with HCl. The most practical method for its formation consists in conducting chlorine gas through SO_4H_2 (15 parts), and gradually adding PCl_3 (7 parts). Or, HCl gas is led into solid fuming sulphuric acid ($S_2O_7H_2$), as long as absorption occurs, and then it is distilled (Otto).

Chlorsulphonic acid is a colorless, strongly fuming liquid of specific gravity 1.776 at 18°, and boils at 155°. Its vapors possess the normal density at a temperature a little beyond the boiling point, but at 180° sustain dissociation, which is complete at 440°, and corresponds to the equation:—

$$2SO_3ClH = SO_3 + H_2O + SO_2 + Cl_2.$$

The salt $SO_2\begin{cases}Cl\\OK\end{cases}$ results from the union of SO_3 with KCl.

The *second chloranhydride*, SO_2Cl_2, or *Sulphuryl-chloride** forms when PCl_5 acts upon SO_3; by heating SO_3HCl to 180°: $2SO_3HCl = SO_2Cl_2 + SO_4H_2$; and also by the direct union of SO_2 with Cl_2 in sunlight:—

$$\underset{1\ \text{vol.}}{SO_2} + \underset{1\ \text{vol.}}{Cl_2} = \underset{1\ \text{vol.}}{SO_2Cl_2}.$$

The most convenient method for its formation is to pass equal volumes of sulphur dioxide and chlorine gas into a capacious flask, containing some camphor, which causes the union of the gases to form sulphuryl chloride. A colorless, suffocating,

---

* The group SO_2 combined with 2OH in H_2SO_4, is known as *Sulphuryl.*

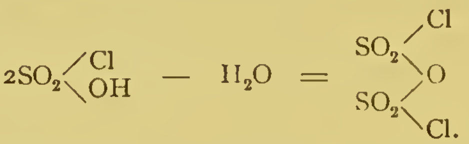
strongly fuming liquid, of specific gravity 1.708 at 0°, results. It boils at 70°. Water decomposes it energetically into sulphuric and hydrochloric acids (also the case with chlorsulphonic acid). A little water will first change it to chlorsulphonic acid:—

$$SO_2\begin{matrix}\diagup Cl\\ \diagdown Cl\end{matrix} + H_2O = SO_2\begin{matrix}\diagup Cl\\ \diagdown OH\end{matrix} + HCl.$$

Its vapor density is normal at 184°; at higher temperatures it gradually diminishes, and at 440° corresponds to the decomposition equation:—

$$SO_2Cl_2 = SO_2 + Cl_2.$$

Pyrosulphuryl Chloride, $S_2O_5Cl_2$, is the chloranhydride of pyrosulphuric acid. It is obtained by several reactions, chiefly, however, by the action of PCl_5 or P_2O_5 upon chlorsulphonic acid:—



$$2SO_2\begin{matrix}\diagup Cl\\ \diagdown OH\end{matrix} - H_2O = \begin{matrix} & \diagup Cl\\ SO_2 & \\ & \diagdown \\ & \quad O\\ & \diagup \\ SO_2 & \\ & \diagdown Cl.\end{matrix}$$

It is a thick liquid, fuming in the air; has a specific gravity = 1.858 at 0°, and, when perfectly pure, boils at 153°. At 183–210° it shows a normal density; it is dissociated at higher temperatures, and this is complete at 440°, corresponding to the equation:—

$$S_2O_5Cl_2 = SO_3 + SO_2 + Cl_2.$$

It dissolves gradually in water, without hissing, and decomposes into SO_4H_2 and HCl; it at first yields chlorsulphonic acid with a little water.

Thionyl chloride—$SOCl_2$—(p. 189) may be regarded as a chloranhydride of sulphurous acid.

POLYTHIONIC ACIDS.

By this name (from θεῖον, sulphur) are understood the complex acids of sulphur, containing two or more atoms of the latter. The following are known:—

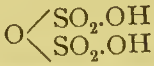
$S_2O_3H_2$ — Thiosulphuric acid.
$S_2O_6H_2$ — Dithionic acid.
$S_3O_6H_2$ — Tri " "
$S_4O_6H_2$ — Tetra " "
$S_5O_6H_2$ — Penta " "

The general chemical character of these acids is represented simply and distinctly in the following structural formulas. We suppose that they contain one or two univalent groups, SO_3H, or

— $\overset{\mathrm{VI}}{\mathrm{S}}\mathrm{O_2OH}$, in which one affinity of sulphur is unsaturated. This group is known as the *sulpho* group; it is also present in organic sulpho-acids, and corresponds to the acid-forming carbon group, COOH, called *carboxyl*. From this group (written in another form) are derived the above-observed acids:—

$H.SO_2.OH$
Sulphurous acid.

$HO.SO_2.OH$
Sulphuric acid.

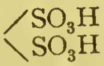


$$\mathrm{O}\left\langle\begin{matrix}\mathrm{SO_2.OH}\\ \mathrm{SO_2.OH}\end{matrix}\right.$$

Disulphuric acid.

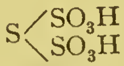
The constitution of the polythionic acids is expressed by the following formulas:—

$HS.SO_3H$
Thiosulphuric acid.



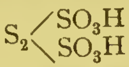
$$\left\langle\begin{matrix}\mathrm{SO_3H}\\ \mathrm{SO_3H}\end{matrix}\right.$$

Dithionic acid.



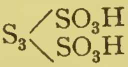
$$\mathrm{S}\left\langle\begin{matrix}\mathrm{SO_3H}\\ \mathrm{SO_3H}\end{matrix}\right.$$

Trithionic acid.



$$\mathrm{S_2}\left\langle\begin{matrix}\mathrm{SO_3H}\\ \mathrm{SO_3H}\end{matrix}\right.$$

Tetrathionic acid.



$$\mathrm{S_3}\left\langle\begin{matrix}\mathrm{SO_3H}\\ \mathrm{SO_3H}\end{matrix}\right.$$

Pentathionic acid.

The last three acids may be viewed as derivatives of the hydrogen sulphides, SH_2, S_2H_2, and S_3H_2, in which both H atoms are replaced by two univalent sulpho groups. In thiosulphuric acid, only 1 H-atom is replaced by *sulpho;* the dithionic acid, on the other hand, results by the direct union of two sulpho groups, with their free affinities.

Thiosulphuric Acid, $H_2S_2O_3 = SO_2\left\langle\begin{matrix}SH\\ OH\end{matrix}\right.$, generally known as *hyposulphurous acid*, can be considered as sulphuric acid in which the oxygen of an hydroxyl group is replaced by sulphur. It is not known in a free condition, since as soon as it is liberated from its salts by stronger acids, it at once decomposes into SO_2, S and H_2O:—

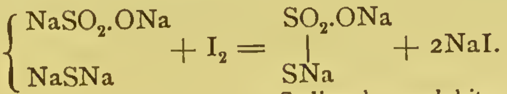
$$S_2O_3Na_2 + 2HCl = 2NaCl + SO_2 + S + H_2O.$$

Its salts, called *hyposulphites*, are of practical importance (compare sodium hyposulphite). They are formed by the direct addition of sulphur to sulphites:—

$$Na_2SO_3 + S = Na_2S_2O_3;$$

similar to the formation of sulphates by the addition of O to the sulphites.

A very interesting formation of thiosulphuric acid is that of the action of iodine upon a mixture of sodium sulphite and sodium sulphide:—



$$\left\{\begin{matrix}\mathrm{NaSO_2.ONa}\\ \mathrm{NaSNa}\end{matrix}\right. + \mathrm{I_2} = \begin{matrix}\mathrm{SO_2.ONa}\\ |\\ \mathrm{SNa}\end{matrix} + 2\mathrm{NaI}.$$

Sodium hyposulphite.

Conversely sodium hyposulphite is split up by sodium amalgam into SO_3Na_2 and Na_2S.

Dithionic Acid—$H_2S_2O_6$—is only known in aqueous solution. When concentrated *in vacuo* or when heated it decomposes into sulphuric acid and sulphur dioxide. Its manganese salt results from the action of sulphur dioxide upon MnO_2 suspended in water:—

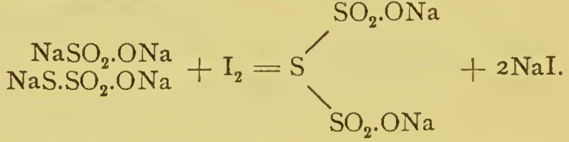
$$MnO_2 + 2SO_2 = MnS_2O_6.$$

Barium hydroxide converts this into the barium salt, from which the free dithionic acid is obtained by means of sulphuric acid. It is very doubtful whether dithionic acid is produced by the action of an iodine solution upon primary sodium sulphite, $NaSO_2.OH$ (Spring).

Trithionic Acid—$H_2S_3O_6$—is not known in a free condition. Its salts are produced when an aqueous solution of primary potassium sulphite is digested with flowers of sulphur:—

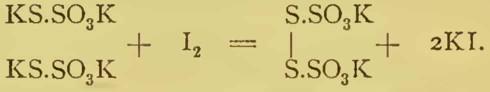
$$6HKSO_3 + 2S = 2K_2S_3O_6 + K_2S_2O_3 + 3H_2O.$$

Separated from its salts by other acids it decomposes into H_2SO_4, SO_2 and S. Its production by the action of iodine upon a mixture of sodium sulphite and hyposulphite is especially interesting:—



$$\begin{matrix} NaSO_2.ONa \\ NaS.SO_2.ONa \end{matrix} + I_2 = S\begin{matrix} \diagup SO_2.ONa \\ \\ \diagdown SO_2.ONa \end{matrix} + 2NaI.$$

Tetrathionic Acid—$H_2S_4O_6$. Its salts are produced when iodine acts upon solutions of the hyposulphites:—



$$\begin{matrix} KS.SO_3K \\ \\ KS.SO_3K \end{matrix} + I_2 = \begin{matrix} S.SO_3K \\ | \\ S.SO_3K \end{matrix} + 2KI.$$

Potassium tetrathionate.

This reaction is applied in volumetric analysis for the quantitative determination of iodine, and such substances as separate iodine from potassium iodide (see sodium thiosulphate).

The tetrathionic acid, separated from its salts by stronger acids, is very unstable, and when its aqueous solution is concentrated it decomposes into sulphuric acid, sulphur dioxide, and sulphur. An aqueous solution of the acid can be easily prepared by conducting hydrogen sulphide into aqueous sulphurous acid:—

$$4SO_2 + 3H_2S = S_4O_6H_2 + 2H_2O + 3S.$$

If the solution be saturated with bases, neutral and acid tetrathionates result, *e.g.*, $S_4O_6Ba + 2H_2O$ and $(S_4O_6H)_2Zn$.

Pentathionic Acid, $S_5O_6H_2$, is supposed to be produced together with the tetrathionic acid when hydrogen sulphide acts upon aqueous sulphurous acid. Later researches, however, have proved that its supposed salts are identical with the acid tetrathionates (Curtius). Another method of production is supposed to be that in which sulphur chloride acts upon barium hyposulphite:—

$$S_2Cl_2 + Ba\,(S.SO_3)_2\,Ba = S\,(S.SO_3)_2\,Ba + BaCl_2 + S.$$

It is, however, doubtful whether pentathionic acid is produced in this reaction.

The polythionic acids are distinguished from sulphuric acid by the solubility of their barium salts.

Amide Derivatives of the Sulphuric Acids.—Different nitrogenous compounds, which must be regarded as derivatives of ammonia and hydroxylamine (p. 131), result upon introducing sulpho-groups, $SO_2.OH$, for amide hydrogen:—

$H_2N.SO_3H$
Amido sulphonic acid, or sulphaminic acid.

$HN(SO_3H)_2$
Imidosulphonic acid, or disulphimidic acid.

$N(SO_3H)_3$
Nitrilo-sulphonic acid.

$HO.NH.SO_3H.$
Hydroxylamine sulphonic acid.

$HO.N(SO_3H)_2$
Hydroxylamine disulphonic acid.

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2. OXYGEN DERIVATIVES OF SELENIUM AND TELLURIUM.

SeO_2
Selenium dioxide.

(SeO_3)
Selenium trioxide.

SeO_3H_2
Selenious acid.

SeO_4H_2
Selenic acid.

Selenium Dioxide—SeO_2, or selenious anhydride, is produced when selenium burns in the air or in oxygen. It consists of long white needles, which sublime at about 320° without fusing. It dissolves readily in water, forming **selenious acid**, H_2SeO_3. The latter is also obtained by dissolving the metal in concentrated nitric acid. When the solution is evaporated it crystallizes in large, colorless prisms, which decompose, on heating, into the anhydride and water. Sulphurous oxide reduces selenious acid, with separation of free selenium:—

$$H_2SeO_3 + 2SO_2 + H_2O = 2H_2SO_4 + Se.$$

Selenic Acid—H_2SeO_4—is obtained by conducting chlorine gas into an aqueous solution of selenious acid:—

$$H_2SeO_3 + H_2O + Cl_2 = H_2SeO_4 + 2HCl.$$

The solution may be concentrated until it attains a specific gravity of 2.6 when it becomes an oily liquid, similar to sulphuric acid, and contains 95 per cent. H_2SeO_4. If the solution be heated above 280°, the acid breaks up into SeO_2, O and H_2O.. Selenic anhydride is unknown.

The salts of selenic acid are known as *selenates*, those of selenious acid as *selenites*.

The derivatives of tellurium are analogous to those of selenium. The dioxide —TeO_2—results when tellurium is burned, and forms a white crystalline mass, fusing at a red heat and subliming. It is almost insoluble in water.

Tellurous Acid—H_2TeO_3—is produced when the metal is dissolved in concentrated nitric acid. Water will precipitate it from such a solution in the form of a white amorphous powder. On warming it readily decomposes into TeO_2 and water.

Telluric Acid—H_2TeO_4. Potassium tellurate is produced when tellurium or its dioxide is fused with saltpetre. The acid (telluric) is obtained from this salt by means of sulphuric acid, and crystallizes from its aqueous solution, in large colorless prisms, with 2 molecules of H_2O ($H_2TeO_4 + 2H_2O$), which are expelled at 100° C., and the acid remains in the form of a white powder. The latter is not very soluble in water, and manifests but a slight acid reaction. When carefully heated, the acid breaks up into water, and the trioxide TeO_3, which is a yellow mass insoluble in H_2O, and by further application of heat decomposes into TeO_2 and oxygen.

The affinity of the elements of the oxygen group for the halogens seems to increase with rise of atomic weight from oxygen to tellurium. This is just the reverse of what we observed for the halogens with hydrogen; OCl_2 is very unstable and is formed with heat absorption; SCl_2 and SCl_4 only exist at lower temperatures, while $SeCl_4$, $TeCl_2$, and $TeCl_4$ even exist as gases. The oxygen derivatives of sulphur, selenium, and tellurium appear to conduct themselves similarly. The thermo-chemical relations, however, show that the gradation is not complete, but that the heat of formation of the derivatives of sulphur is greater than that of those of selenium—as is the case in the chlorine group (p. 185). This may be seen in the heat of formation of the anhydrous dioxides:—

$$(S,O_2\text{-gas}) = 71.0. \quad (Se,O_2)\text{-solid} = 57.7,$$

and also in that of the acids from their elements and water (page 189):—

$(S,O_2,Aq.) = 78.7$ $(Se,O_2,Aq.) = 56.7$ $(Te,O_2,Aq.) = 81.2$
$(S,O_3,Aq.) = 142$ $(Se,O_3,Aq.) = 77.2$ $(Te,O_3,Aq.) = 107.0$

In all these compounds, consequently, the affinity of selenium to oxygen is the least, and this explains the reduction of selenious by sulphurous acid, as well as the slight stability of selenic acid.

OXYGEN DERIVATIVES OF THE ELEMENTS OF THE NITROGEN GROUP.

The halogens combine with one atom of hydrogen and also afford oxygen acids containing one atom of H. The elements of the sulphur group contain two atoms of H in the hydrogen derivatives and oxygen acids. In accord with this we find that the elements of the N group combine with three atoms of H, and form acids which also contain three atoms of the same element:—

HCl	H_2S	PH_3
$HClO_4$ Perchloric acid.	H_2SO_4 Sulphuric acid.	PO_4H_3 Phosphoric acid.
$HClO_3$ Chloric acid.	H_2SO_3 Sulphurous acid.	PO_3H_3 Phosphorous acid.

The acids containing three atoms of H, designated *normal* or *Ortho-Acids* (as H_3PO_4, H_3AsO_4, H_3AsO_3) can yield monobasic acids by the removal of one molecule of water. Such derivatives, having one atom of H, are called *meta-acids:*—

H_3PO_4 Orthophosphoric acid.	HPO_3 Metaphosphoric acid.
H_3AsO_3 Orthoarsenious acid.	$HAsO_2$ Metaarsenious acid.

These meta-acids of phosphorus and arsenic are less stable than the ortho-acids and pass into the latter by the absorption of water. The ortho-acids of N, on the other hand, are less stable and only exist in some salts. The ordinary acids and salts of N belong to the meta-series and contain one atom of H (or metal):—

(H_3NO_4) Orthonitric acid.	HNO_3 Ord. Nitric acid.
(H_3NO_3) Orthonitrous acid.	HNO_2 Ord. Nitrous acid.

The further exit of water affords the true anhydrides (p. 178).

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1. OXYGEN DERIVATIVES OF NITROGEN.

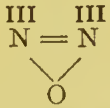
N_2O_5 Nitrogen pentoxide.	NO_3H Nitric acid.
N_2O_3 Nitrogen trioxide.	NO_2H Nitrous acid.
N_2O Hyponitrous oxide.	$(NOH)_2$ Hyponitrous acid.

In addition to the above compounds we have: *Nitrogen tetroxide* (N_2O_4), the mixed anhydride of nitrous and nitric acids, and two oxides, *nitrogen dioxide* (NO_2) and *nitric oxide* (NO), which do not yield acids.

The following formulas express the structure of these compounds:—

$$N \equiv N$$

Nitrogen.



$$\overset{III}{N} = \overset{III}{N} \quad O$$

Hyponitrous oxide.

$$\overset{III}{ON} - O - \overset{III}{NO}$$

Nitrogen trioxide.

$$\overset{V}{O_2N} - O - \overset{V}{NO_2}$$

Nitrogen pentoxide.

$$\overset{V}{O_2N} - OH$$

Nitric acid.

$$\overset{III}{ON} - OH$$

Nitrous acid.

$$(\overset{III}{ON} - H)_2$$

Hyponitrous acid.

$$\overset{III}{ON} - O - \overset{V}{NO_2}$$

Nitrous-Nitric anhydride.

The salts of nitric acid are called *nitrates;* those of nitrous, *nitrites.*

NITRIC ACID.—HNO_3.

This acid occurs in nature only in the form of salts,—potassium, sodium, and calcium nitrates (compare these)—which have resulted from the decay of nitrogenous organic substances in the presence of strong bases (the alkalies). It is sometimes present in the air as ammonium salt. The free acid is formed in very slight quantity by conducting the electric sparks through moist air.

To prepare nitric acid heat potassium or sodium nitrate with sulphuric acid, when the nitric acid will distil over and sodium sulphate remain:—

$$2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3 \text{ and}$$
$$NaNO_3 + H_2SO_4 = HNaSO_4 + HNO_3.$$

This process may be conducted in the distillation apparatus figured on page 53. The quantity, by weight, of sodium nitrate and sulphuric acid corresponding to the second equation must be employed, because with less acid a higher temperature is requisite to complete the reaction, and, in consequence, the nitric acid that is produced will be partially decomposed.

Pure anhydrous nitric acid is a colorless liquid of specific gravity 1.54 at 0°, fumes in the air, and at —40° solidifies to a crystalline mass. At ordinary temperatures it undergoes a partial decomposition (like H_2SO_4) into water, oxygen, and nitrogen dioxide, NO_2, which dissolves in the acid, with a yellowish-brown color; the colorless acid therefore becomes colored upon standing, and in sunlight soon turns yellow. At 86° the acid commences boiling and sustains a partial decomposition; the first portions are colored yellow by the dissolved nitrogen dioxide, but subsequently, some aqueous acid distils over. Nitric acid is completely decomposed into nitrogen dioxide, oxygen, and water, when its vapors are conducted through red-hot tubes:—

$$2HNO_3 = 2NO_2 + H_2O + O.$$

The acid mixes in all proportions with water. Upon distilling the dilute aqueous solution, only pure water passes over at first; the boiling temperature gradually rises, and at 121° a solution goes over, which contains 68 per cent. HNO_3, and has a specific gravity of 1.414 at 15°. This is the ordinary concentrated nitric acid of trade. When this is distilled with 5 parts sulphuric acid, an almost anhydrous acid is obtained, which may be freed of NO_2 contained in it by conducting a stream of air through it.

Generally, the anhydrides of acids distil at temperatures lower than the acids themselves (SO_3 is more volatile than H_2SO_4). The higher boiling-point of the aqueous nitric acid, in relation to the anhydrous, is probably explained by the fact that the hydrate $HNO_3 + H_2O$, *i. e.*, the normal nitric acid, $NO_4H_3 = NO(OH)_3$ (p. 205), is present in this solution. The liquid boiling at 121°, however, contains more water than corresponds to this hydrate (just as distilled sulphuric acid contains water), so that it can be regarded as a mixture of the trihydrate ($NO(OH)_3$) and pentahydrate ($N(OH)_5$).

Nitric acid is a very powerful acid, oxidizing or dissolving almost all metals (gold and platinum excepted). Nearly all the metalloids, like sulphur, phosphorus, and carbon, are converted by it into their corresponding acids. It acts as a very strong oxidizing agent, destroying organic coloring substances, and decolorizes a solution of indigo very readily. In so doing the nitric acid itself is deoxidized to the lower oxidation products of nitrogen (NO and NO_2). Some substances even reduce the acid to ammonia. Thus, for example, if zinc be brought into dilute nitric acid (5–6 per cent.) the metal will be dissolved without the liberation of hydrogen. The latter, *in statu nascendi*, acts at once upon the excess of acid and reduces it to ammonia, which forms an ammonium salt with the acid; hence, in solution, we have ammonium nitrate in addition to the zinc nitrate:—

$$2HNO_3 + Zn = Zn(NO_3)_2 + H_2 \text{ and}$$
$$2HNO_3 + 4H_2 = NO_3NH_4 + 3H_2O.$$

If the aqueous nitric acid be less dilute (containing more than 10 per cent. NO_3H) it will be reduced by zinc and other metals, not to ammonia, but to the nitrogen oxides, N_2O, NO, N_2O_3, and N_2O_4. The more concentrated the acid, the higher will the oxides be.

The reduction of nitric acid to ammonia by nascent hydrogen occurs more easily in alkaline solution. If an alkaline solution of nitrates be treated with zinc or aluminium filings, all the N of the nitric acid will be converted into ammonia:—

$$HNO_3 + 4H_2 = NH_3 + 3H_2O.$$

Hydroxylamine (p. 131) and ammonia are produced when nitric acid acts on tin.

Nitric acid—NO_2OH—and its hydrates, $NO(OH)_3$ and $N(OH)_5$ (see above), usually form salts of the form NO_3Me, with 1 eq. of the metals; these are called nitrates, and are all soluble in water.

Red Fuming Nitric Acid (*Acidum Nitricum Fumans*) is the name given a nitric acid containing much nitrogen dioxide in solution. It is obtained by the distillation of 2 molecules of KNO_3 with 1 molecule of sulphuric acid (p. 206), or better, by the distillation of commercial nitric acid with much sulphuric acid. It generally has the specific gravity 1.5–1.54, and possesses greater oxidizing power than the colorless nitric acid.

A mixture of 1 volume nitric acid and 3 volumes concentrated hydrochloric acid is known as *aqua regia,* as it is able to dissolve gold and platinum, which neither of the acids alone is capable of doing. The powerful oxidizing action of the mixture is due to the presence of free chlorine and the two chlorine derivatives (NO_2Cl and $NOCl$), which may be considered the chloranhydrides of nitric and nitrous acids.

Nitrogen Pentoxide—N_2O_5—nitric anhydride, is produced when phosphoric anhydride acts on nitric acid:—

$$2HNO_3 + P_2O_5 = N_2O_5 + 2HPO_3;$$

further, by conducting nitroxyl chloride over silver nitrate:—

$$AgO.NO_2 + NO_2Cl = \left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\}O + AgCl.$$

It forms colorless, rhombic prisms, fusing at 30° and boiling with partial decomposition at 47°. It is very unstable, decomposing readily into N_2O_4 and O, and sometimes exploding spontaneously. It yields HNO_3 with water and evolves much heat by the union:—

$$\left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\}O + H_2O = 2NO_2OH.$$

Nitroxyl Chloride—NO_2Cl—the chloranhydride of nitric acid, results by the union of NO_2 with chlorine, and according to the ordinary method of forming chloranhydrides (see p. 199), by the action of PCl_5 or $POCl_3$ upon nitric acid, or better, its silver salt:—

$$\underset{\text{Silver nitrate.}}{3NO_2OAg} + POCl_3 = \underset{\text{Silver phosphate.}}{PO(OAg)_3} + 3NO_2Cl.$$

Recent investigations make its existence questionable.

Nitrosyl Chloride—$NOCl$—is produced by the union of NO (2 volumes) with chlorine (1 volume): $2NO + Cl_2 = 2NOCl$, and when phosphoric chloride, PCl_5, is allowed to act upon liquid nitrogen tetroxide, N_2O_4, in the cold. The reddish yellow vapors that escape, if cooled to —20°, condense to a red liquid of sp. gr. 1.416 at —12°, and boiling at +2°. It is a reddish-yellow gas which below 0° condenses to a liquid. It forms nitrous and hydrochloric acids with water:—

$$NOCl + H_2O = HNO_2 + HCl.$$

It may, therefore, be regarded as the chloranhydride of nitrous acid—$NO.OH$.

Nitrogen Trioxide—N_2O_3—nitrous anhydride, is formed by the direct union of nitrogen oxide (4 volumes) with oxygen (1 volume) at —18°:—

$$\underset{4\text{ vols.}}{4NO} + \underset{1\text{ vol.}}{O_2} = \underset{2\text{ vols.}}{2N_2O_3};$$

by mixing liquid nitrogen tetroxide, N_2O_4, with a little cold water:—

$$2\left.\begin{matrix}NO_2\\NO\end{matrix}\right\}O \quad + \quad H_2O \quad = \quad \left.\begin{matrix}NO\\NO\end{matrix}\right\}O \quad + \quad 2NO_2.OH;$$

by the introduction of nitric oxide into liquid nitrogen tetroxide:—

$$N_2O_4 + 2NO = 2N_2O_3;$$

and by conducting nitric oxide into anhydrous nitric acid:—

$$2NO_3H + 4NO = 3N_2O_3 + H_2O.$$

It is most easily obtained by the action of nitric acid upon arsenious acid, As_2O_3. Nitrogen tetroxide is simultaneously produced, from which it is readily separated by fractional distillation and condensation.

Nitrogen trioxide condenses at —20° to a dark-blue liquid of 1.449 sp. gr. at 0°, and boils at +4°. It decomposes when distilled; its vapors consist of a mixture of the tetroxide and nitric oxide ($N_2O_4 + 2NO$). Upon cooling they re-unite to the liquid nitrous anhydride. The latter is therefore only known in the liquid condition (Geuther).

The trioxide mixed with a little cold water probably forms nitrous acid (HNO_2); more water, aided by heat, decomposes it into nitric acid and nitric oxide gas:—

$$3NO_2H = HNO_3 + 2NO + H_2O.$$

Nitrous Acid, HNO_2, is not known in a free state. Its salts (the nitrites) are obtained by igniting the nitrates:—

$$KNO_3 = KNO_2 + O.$$

The withdrawal of oxygen is rendered easier if oxidizable metals, *e. g.*, lead, be added to the fusion.

On adding sulphuric acid to the nitrites, brown vapors are disengaged; these consist of NO_2 and NO. It may be that the nitrous acid, at first liberated, is broken up into water and the trioxide, which, as we have seen above, gradually decomposes into NO_2 and NO. Similar reddish-brown vapors are obtained if nitric acid be permitted to act upon starch or arsenious oxide (As_2O_3).

According to Lunge, if we employ nitric acid of 1.30–1.35 sp. gr., nitrogen trioxide is produced almost exclusively, whereas in using the concentrated acid (1.4–1.5) we get a mixture of N_2O_3 and N_2O_4, and chiefly NO, with a little N_2O_3, if the acid be dilute.

The nitrous acid that has separated out in the solution and its decomposition products—NO_2 and NO—are strong oxidizers, setting iodine free from the soluble iodides. In other cases, however, they exhibit a reducing action ; thus, *e. g.*, the acidified red solution of potassium permanganate is decolorized by the addition of nitrites. In very dilute solution, the action proceeds according to the following equation :—

$$5NO_2H + 2MnO_4K + 3SO_4H_2 = 5NO_3H + SO_4K_2 + 2SO_4Mn + 3H_2O.$$

This reaction serves for the determination of free nitrous acid, as well as for its salts (p. 212).

Nitrogen Tetroxide—N_2O_4 or *nitrogen dioxide* NO_2 (formerly called *hyponitric acid*), really constitutes two compounds. The former only exists at low temperatures ; when heated, it suffers a gradual decomposition into the simpler molecules NO_2 which recombine to N_2O_4 upon cooling. We here meet the interesting case of dissociation, occurring even at the ordinary temperature. N_2O_4 is colorless, while NO_2 is colored red-brown ; it appears, therefore, that the color gradually becomes darker as the temperature rises, and that it corresponds to the increasing dissociation of the complex molecules N_2O_4.

At ordinary temperatures, nitrogen tetroxide is a yellow liquid of sp. gr. 1.45 at 15°. When cooled to —20° it solidifies to a colorless crystalline mass, melting at —12°. In consequence of the dissociation that sets in at 0°, the liquid, at first colorless, becomes yellow, and the intensity in color grows with rising temperature. The liquid begins to boil at about 26°, and is converted into a yellowish-brown vapor that becomes dark as the temperature is increased.

The theoretical vapor density of N_2O_4 (molecular weight $= 91.86$) equals 45.9, while that of NO_2 $(45.9) = 22.9$. The experimental vapor density has been found to equal 38 at the point at which the liquid compound boils (26°) ; it may be calculated from this that, at this temperature, 34.4 per cent. of the N_2O_4 molecules are decomposed into NO_2 molecules. Hence we conclude that the dissociation of the compound N_2O_4 commences already in the liquid state; this is confirmed by the yellow coloration appearing at 0°. Sulphuric acid, as we saw (p. 196), exhibits a similar dissociation in liquid condition. With rising temperature the density of the vapor steadily diminishes, becomes constant finally at 150° and equals 22.9. Then all the molecules (N_2O_4) are decomposed into the simpler molecules NO_2 ; and the dark coloration of the vapors attains its maximum.

Nitrogen tetroxide is formed by the union of two volumes of nitric oxide with one volume of oxygen :—

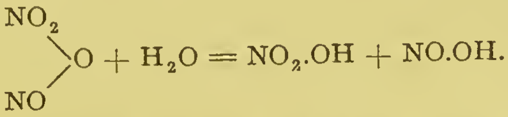
$$\underset{\text{2 vols.}}{2NO} + \underset{\text{1 vol.}}{O_2} = \underset{\text{1 vol.}}{N_2O_4}.$$

We can get it more conveniently by heating dry lead nitrate, which decomposes according to the following equation :—

$$(NO_3)_2Pb = PbO + O + 2NO_2.$$

The escaping vapors condense in the cooled receiver to liquid N_2O_4.

The varying molecular composition of nitrogen tetroxide at lower and higher temperatures manifests itself also in its chemical reactions. We saw that by the action of a little cold water, the tetroxide was decomposed into nitrogen trioxide and nitric acid (p. 209). With excess of cold water, and also with an aqueous solution of alkalies, it yields nitric and nitrous acids, that is, their salts:—



$$\left.\begin{matrix}NO_2\\ NO\end{matrix}\right\rangle O + H_2O = NO_2.OH + NO.OH.$$

Both reactions plainly indicate that the liquid tetroxide represents the *mixed oxide* of nitric and nitrous acids; similarly, the compound Cl_2O_4 constitutes the mixed oxide of chloric and chlorous acids (p. 181).

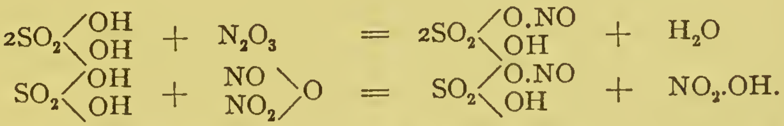
Warm water converts the tetroxide into the dioxide, NO_2, which in turn yields nitric acid and nitric oxide:—

$$3NO_2 + H_2O = 2HNO_3 + NO.$$

The tetroxide and dioxide possess strong oxidizing properties; many substances burn in their vapors; iodine is set free from the soluble metallic iodides by them.

Nitrosylsulphuric Acid, $SO_5NH = SO_2\left\langle\begin{matrix}O.NO.\\ OH.\end{matrix}\right.$

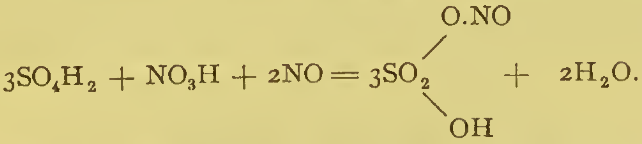
This compound, termed nitrosulphonic acid, is an intermediate product in the manufacture of commercial sulphuric acid (see p. 194), and is quite important. It is employed in the analytical determination of the nitrogen oxides. It is produced by conducting nitrogen trioxide and tetroxide into concentrated sulphuric acid:—



$$2SO_2\left\langle\begin{matrix}OH\\ OH\end{matrix}\right. + N_2O_3 = 2SO_2\left\langle\begin{matrix}O.NO\\ OH\end{matrix}\right. + H_2O$$

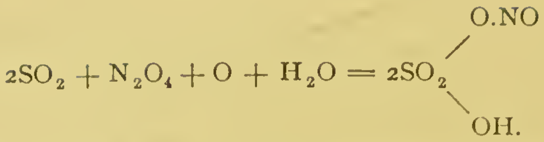
$$SO_2\left\langle\begin{matrix}OH\\ OH\end{matrix}\right. + \left.\begin{matrix}NO\\ NO_2\end{matrix}\right\rangle O = SO_2\left\langle\begin{matrix}O.NO\\ OH\end{matrix}\right. + NO_2.OH.$$

Nitrogen monoxide—NO—is not absorbed by pure sulphuric acid, but will be if the same contains nitric acid:—



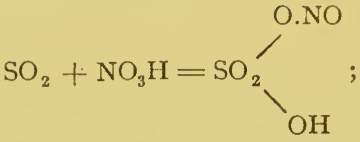
$$3SO_4H_2 + NO_3H + 2NO = 3SO_2\left\langle\begin{matrix}O.NO\\ OH\end{matrix}\right. + 2H_2O.$$

Further, the nitrosylsulphuric acid results from the combined action of sulphurous oxide, nitrogen tetroxide (or trioxide), oxygen, and a little water:—



$$2SO_2 + N_2O_4 + O + H_2O = 2SO_2\left\langle\begin{array}{l}O.NO\\OH.\end{array}\right.$$

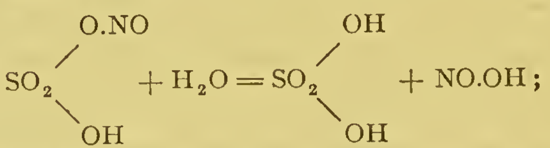
It is obtained most readily by conducting sulphur dioxide into strongly cooled anhydrous nitric acid :—



$$SO_2 + NO_3H = SO_2\left\langle\begin{array}{l}O.NO\\OH\end{array}\right. ;$$

there results a thick magma, which may be dried upon porous earthen plates under the desiccator.

Nitrosylsulphuric acid forms a leafy or granular crystalline, colorless mass (chamber-acid crystals, p. 195), which fuses about 73° and decomposes into its anhydride, sulphuric acid, and nitrogen trioxide. It deliquesces in moist air, and yields sulphuric and nitrous acids with water :—

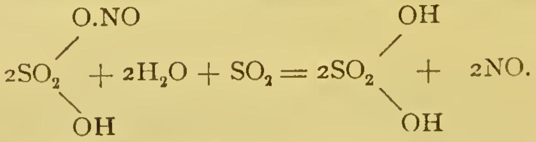


$$SO_2\left\langle\begin{array}{l}O.NO\\OH\end{array}\right. + H_2O = SO_2\left\langle\begin{array}{l}OH\\OH\end{array}\right. + NO.OH ;$$

the nitrous acid decomposes further into nitric acid and nitric oxide.

Nitrosylsulphuric acid dissolves in concentrated sulphuric acid without any change; the solution, called *nitroso acid*, is also produced in the sulphuric acid manufacture in the Gay-Lussac tower, is very stable and may be distilled without decomposition. When diluted with water it remains unaltered at first, but when the specific gravity of the solution reaches 1.55–1.50 (51–48° B), then all the nitrogen oxides escape, especially on warming. When the nitroso acid is poured into a large quantity of water, the nitrososulphuric acid breaks up into (like the pure acid, see above) sulphuric and nitrous acids, and the latter in part into NO_2H and 2NO. Therefore, in titrating nitrous acid with permanganate of potassium (MnO_4K. See p. 210), we get the results corresponding to nitrososulphuric acid, if the latter be poured into the permanganate (Lunge).

All the nitrogen oxides and acids are separated as nitric oxide (NO) on shaking the nitroso acid with mercury—a procedure serving equally well for estimating the amount of nitroso acid by means of the nitrometer. All nitrogen oxides are expelled from the nitroso acid by dilution with water and application of heat (see above). This occurs more readily and completely (even upon concentration to 58° B. = 1.679 specific gravity) by the action of sulphur dioxide :—



$$2SO_2\left\langle\begin{array}{l}O.NO\\OH\end{array}\right. + 2H_2O + SO_2 = 2SO_2\left\langle\begin{array}{l}OH\\OH\end{array}\right. + 2NO.$$

Upon this depends the denitrating action of the *Glover tower*—see p. 195.

The *anhydride* of nitrosulphonic acid—$S_2N_2O_9 = O\left\{\begin{matrix}SO_2.O.NO\\ SO_2.O.NO\end{matrix}\right.$, is produced upon heating the latter (together with SO_4H_2 and N_2O_3—see p. 212) beyond its point of fusion. It is obtained pure by saturating sulphur trioxide with nitric oxide: $3SO_2 + 2NO = O\ (SO_2.O.NO)_2 + SO_2$. It is a crystalline, colorless mass, fusing at 217°, and boiling without decomposition about 360°. Much water decomposes it, the same as nitrosylsulphuric acid.

The *chloranhydride* of nitrosulphonic acid, SNO_4Cl, is formed by the union of sulphur trioxide with nitrosylchloride: $SO_2 + NOCl = SO_2Cl\ (O.NO)$. It forms white leaflets, is decomposed by heat into its components, and with water breaks up into sulphuric, hydrochloric and nitrous acids.

Nitric Oxide—NO. When different metals are dissolved in somewhat dilute nitric acid this oxide is formed, inasmuch as the hydrogen *in statu nascendi* reduces another portion of the acid. It is most conveniently obtained by pouring dilute nitric acid (specific gravity 1.2) upon copper filings:—

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO.$$

A better procedure consists in gradually adding concentrated sulphuric acid to a saturated solution of saltpetre, covering thin copper turnings.

The action begins in the cold. A colorless gas escapes, which, however, immediately forms brown vapors when it comes in contact with the air, as it unites with the oxygen of the latter to form NO_2. Therefore, all the air must be expelled from the generating vessel by NO, and the gas collected over water after the interior of the apparatus has become colorless.

Nitric oxide is a colorless gas, of specific gravity 15 (H = 1) or 1.038 (air = 1). Its gas density remains unaltered at —100° (referred to air of the same temperature, V. Meyer). It is condensed with difficulty. Its critical temperature is —93°, and its critical pressure 71 atmospheres (Olszewski). It is slightly soluble in water, but dissolves very readily in an aqueous solution of ferrous salts, imparting a reddish-brown color to the liquid; heat expels it from the same.

Nitric oxide is readily soluble in nitric acid. As its solution becomes more concentrated, it assumes a brown, yellow, green or blue color, as nitrogen trioxide is formed finally with anhydrous nitric acid:—

$$2HNO_3 + 4NO = 3N_2O_3 + H_2O.$$

Potassium permanganate oxidizes it, like nitrous acid (p. 210), to nitric acid:—

$$10NO + 6MnO_4K + 9SO_4H_2 = 10NO_3H + 3SO_4K_2 + 6SO_4Mn + 4H_2O.$$

As nitric oxide contains 53.3 per cent. oxygen, it is capable of sustaining the combustion of some substances, but to bring about the previous separation of oxygen from the nitrogen requires energetic reaction. Hence, phosphorus continues to burn in this gas, while a sulphur flame, developing only a slight heat, is extinguished; ignited charcoal does the same, while a splinter, burning energetically, will continue to do so, when introduced into the gas. On shaking a cylinder filled with NO with a few drops of readily volatile carbon disulphide, and bringing a flame to the mouth of the vessel, the carbon disulphide vapors will quietly burn in the gas, giving a bright luminous flame, emitting strong actinic rays; in this combustion, the C and S of the CS_2 unite with the oxygen of the nitric oxide.

Nitric oxide is a strongly endothermic compound (see p. 216), and is consequently explosive (p. 29). It may be caused to explode by inflaming a little fulminating mercury in it (Berthelot).

On determining the quantity of heat disengaged in the combustion of phosphorus, carbon or other substances in NO gas, it will be discovered that the same is greater (about 21,600 calories), than that which is developed by the combustion of these bodies in oxygen. This can only be explained upon the theory that less heat is necessary for the separation of NO into N and O than for the separation of the molecules of combined oxygen atoms—an additional proof that the molecules of free oxygen (as of other elements) consist of atoms (p. 116).

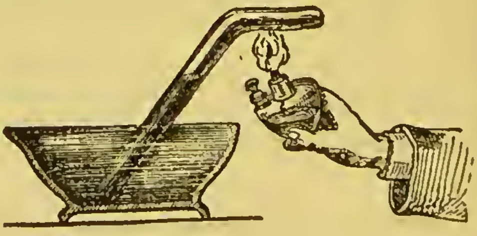
With oxygen or air, NO at once forms brown vapors of nitrogen dioxide:—

$$\underset{\text{2 vols.}}{2NO} + \underset{\text{1 vol.}}{O_2} = \underset{\text{2 vols.}}{2NO_2}.$$

With less oxygen, nitrogen trioxide is produced (p. 208). NO also combines with chlorine to nitrosylchloride, NOCl (p. 208), and the compound $NOCl_2$, which is, as yet, little investigated; with bromine, it yields $NOBr_3$. At a red heat NO becomes NO_2 and N. With hydrogen and moderate heat it forms water and nitrogen: $NO + H_2 = N + H_2O$; a mixture of both gases burns with a white flame. On conducting NO and H together over platinum sponge, water and ammonia are produced:—

$$2NO + 5H_2 = 2NH_3 + 2H_2O.$$

FIG. 85.



The volumetric analysis of nitric oxide gas may be easily executed as follows: Fill a bent glass tube (Fig. 85) over mercury with NO gas; introduce into the same a piece of sodium and heat the latter with a lamp. The sodium combines with the oxygen, and free nitrogen separates; the volume of the latter always equals half the volume of the nitric oxide gas employed; this follows from the formula NO:—

$$\underset{\text{2 vols.}}{2NO} = \underset{\text{1 vol.}}{N_2} + \underset{\text{1 vol.}}{O_2}.$$

The molecular formula of the oxide is $NO = 29.27$ (even at —100°, see p. 210), as its vapor density is 14.98 ($H = 1$). NO, NO_2 and chlorine dioxide, ClO_2 (p. 180), present an apparent anomaly as regards the common laws regulating the valence of the elements. Ordinarily, the valence changes from an odd number to an odd, and from an even to an even number (p. 174). Nitrogen is usually pentavalent and trivalent; in the cited compounds it appears di- and tetravalent. This abnormal behavior of N finds a partial explanation in the position it occupies in the periodic system of the elements.

Nitrous Oxide—*Hyponitrous Oxide*—N_2O—is formed when zinc or tin acts upon dilute nitric acid of sp. gr. 1.1. It may be best obtained by heating ammonium nitrate, which at about 170° breaks up directly into water and nitrous oxide:—

$$NH_4NO_3 = N_2O + 2H_2O.$$

This compound is a colorless gas, of sweetish taste and slight odor. Its density is 22.04 ($H = 1$), or 1.52 (air = 1), corresponding to the molecular formula $N_2O = 44.08$. In cold water it is tolerably soluble (1 volume H_2O dissolves at 0° 1.305 volumes N_2O); therefore it must be collected over warm water or mercury. Cooled to —88°, or under a pressure of 30 atmospheres at 0°, it condenses to a colorless liquid of specific gravity 0.937. By evaporation of the liquid in the air its temperature diminishes to —100°, and it solidifies to a crystalline, snowy mass. If the aqueous nitrous oxide be evaporated under an air pump its temperature falls to —140°; the lowest which has been attained. Although this oxide contains less oxygen than nitric oxide, it supports the combustion of many bodies more readily than the latter, because it is more easily decomposed into oxygen and nitrogen. A glimmering chip inflames in it, as in oxygen; phosphorus burns with a bright, luminous flame, while a sulphur flame is extinguished. The liquid nitrous oxide behaves like the gas; an ignited coal thrown on its surface burns with a bright light. A mixture of equal volumes of nitrous oxide and hydrogen explodes like detonating gas, only less violently:—

$$\underset{\text{1 vol.}}{N_2O} + \underset{\text{1 vol.}}{H_2} = \underset{\text{1 vol.}}{N_2} + H_2O.$$

It resembles oxygen very much, but may be distinguished from it by not producing brown vapors with nitric oxide, as does the former. It is not capable of combining with oxygen. When it is conducted through a red-hot tube it is decomposed into nitrogen and oxygen. It has an exhilarating effect when inhaled in slight quantity, and is, therefore, termed *laughing gas.*

Its volume composition may be determined in the same manner as with nitric oxide, viz.: by heating a definite volume of the gas with potassium. Then we learn that from a volume of N_2O an equal volume of nitrogen will be separated—corresponding to the molecular formula :—

$$\underset{\text{1 vol.}}{N_2O} + K_2 = \underset{\text{1 vol.}}{N_2} + K_2O.$$

Hyponitrous Acid—NOH. As nitrous and nitric acids correspond to nitrogen trioxide and pentoxide, so hyponitrous oxide may be regarded as the anhydride of the recently discovered hyponitrous acid :—

$$N_2O + H_2O = 2NOH,$$

although the latter is not formed by the hydration of N_2O. On the contrary, it yields nitrous oxide when water is withdrawn from it by sulphuric acid.

An aqueous solution of the acid may be obtained by decomposing the silver salt, AgNO, with hydrochloric acid. Dissolved in water it is colorless, reacts strongly acid and is tolerably stable. It liberates iodine from potassium iodide and reduces a permanganate solution. The silver salt is again precipitated by silver nitrate.

The alkali salts of hyponitrous acid result from the action of sodium amalgam upon the nitrates or nitrites, or of freshly precipitated ferrous hydroxide upon sodium nitrite, and by the electrolysis of the nitrites. On neutralizing the solution with acetic or nitric acid, and adding silver nitrate, the silver salt is obtained as a light-yellow amorphous powder, which decomposes gradually at 100°, but with explosive violence at 110°. It is soluble in dilute sulphuric acid, and is reprecipitated upon neutralization with ammonium hydroxide. Concentrated sulphuric acid liberates N_2O from it and the free acid.

The latest researches make the composition of hyponitrous acid rather doubtful, since either the formula N_2O_2Ag or $N_4O_5Ag_4$ may be ascribed to the silver salt.

The thermo-chemical relations of the oxygen derivatives of nitrogen give some clue to their chemical deportment. All nitrogen oxides are endothermic compounds, *i.e.*, they are produced from their elements with heat absorption (compare p. 185) corresponding to the symbols :—

$$(N_2O) = -18.3 \quad (N,O) = -21.5 \quad (N_2O_3) = -23.0 \quad (N,O_2) = -2.0$$
$$(N_2,O_5 - \text{gas}) = -12.0.$$

From this we observe that the oxides of nitrogen cannot be prepared from the elements without addition of energy, and their direct production has never been noticed. Proceeding from nitric oxide (NO), we see from the above numbers that the formation of the higher oxides from it occurs with heat disengagement :—

$$(2NO,O) = 20.1 \quad (NO,O) = 19.5 \quad (2NO_2,O) = 2.8,$$

whereas heat is absorbed in the conversion of nitrous into nitric oxide: $(N_2O,O) = -24.8$. Hence nitric oxide combines readily with oxygen to yield N_2O_3 and NO_2, while nitrous oxide is not reactive. Conversely, the higher oxides are easily reduced to nitric oxide, and this explains their great ability to oxidize. The heat absorption of nitric oxide $(N,O = -21.5)$ indicates, therefore, that the affinity of N to O is so much less than that of the oxygen atoms in the molecule (p. 214).

Heat disengagement, on the contrary, occurs in the production of nitric acid from its elements:—

$$(N,O_3,H \text{ — liquid}) = 41.5 \quad (N,O_3,H,Aq.) = 49.0.$$

This explains the relative stability of that acid, and the possibility of its production under different conditions.

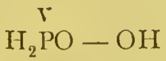
2. OXYGEN COMPOUNDS OF PHOSPHORUS.

......	PO_2H_3 Hypophosphorous acid.
P_2O_3 Phosphorus trioxide.	PO_3H_3 Phosphorous acid.
P_2O_5 Phosphorus pentoxide.	PO_4H_3 Orthophosphoric acid.

The following anhydride acids (compare p. 204) are derived from orthophosphoric acid:—

HPO_3 — Metaphosphoric acid.
$H_4P_2O_7$ — Pyrophosphoric acid.

The structure of these compounds is expressed by the following formulas:—

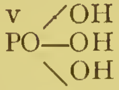


$H_2\overset{\mathrm{v}}{P}O - OH$

Hypophosphorous acid.

$H\overset{\mathrm{v}}{P}O\begin{cases} OH \\ OH \end{cases}$

Phosphorous acid.



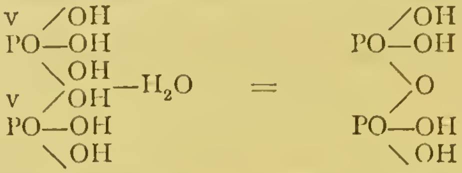
$\overset{\mathrm{v}}{P}O\begin{cases} OH \\ OH \\ OH \end{cases}$

Phosphoric acid.

In hypophosphorous acid two atoms of hydrogen are directly combined with pentavalent phosphorus, while the third atom forms an hydroxyl group with oxygen. The latter is easily replaced by the action of bases, and, therefore, hypophosphorous acid is a *monobasic acid.* Phosphorous acid contains one atom of H united to P and two hydroxyl groups; therefore, it is *dibasic.* Finally, phosphoric acid has three hydroxyl groups, and forms three series of salts. By the elimination of one molecule of H_2O from H_3PO_4, metaphosphoric acid results—an anhydride, which, at the same time, is a monobasic acid, as it contains one hydroxyl group:—

$$\overset{\mathrm{v}}{P}O_2 - OH \text{ — Metaphosphoric acid.}$$

On removing one molecule of H_2O from two molecules of H_3PO_4, pyro- or diphosphoric acid is formed (see p. 197):—



2 Molecules Phosphoric acid. 1 Molecule Diphosphoric acid.

Pyrophosphoric acid contains 4 hydroxyl groups, hence is tetrabasic.

Finally, if from two molecules of phosphorous acid or phosphoric acid, all the H atoms be removed, in the form of water, two perfect anhydrides are obtained:—

$$\overset{\mathrm{III}}{OP}-O-\overset{\mathrm{III}}{PO} \quad \text{and} \quad O_2\overset{\mathrm{V}}{P}-O-\overset{\mathrm{V}}{P}O_2$$

Phosphorous anhydride. Phosphoric anhydride.

The salts of phosphoric acid are termed *phosphates;* those of phosphorous acid, *phosphites*, and of hypophosphorous acid, *hypophosphites.*

Hypophosphorous Acid—H_3PO_2. Hydrogen phosphide escapes when a concentrated solution of sodium or barium hydroxide is warmed with yellow phosphorus, leaving behind in solution a salt of hypophosphorous acid:—

$$4P + 3NaOH + 3H_2O = 3H_2PO.ONa + PH_3.$$

The free acid may be separated from the barium salt by means of sulphuric acid; the insoluble barium sulphate being filtered off from the aqueous solution of the acid, and the latter concentrated under the air-pump. Hypophosphorous acid is a colorless, thick liquid, with a strong acid reaction. Below 0° it sometimes solidifies to large white leaflets, which fuse at + 17.4°. Heat converts it, with much foaming, into hydrogen phosphide and phosphoric acid:—

$$2PO_2H_3 = PH_3 + PO_4H_3.$$

It absorbs oxygen readily, becoming phosphoric acid, hence acts as a powerful reducing agent. It reduces sulphuric acid to sulphur dioxide, and even to sulphur. It precipitates many of the metals from their solutions; from copper sulphate it separates the hydride —Cu_2H_2.

The acid is monobasic, $H_2PO.OH$. Its salts dissolve readily in water, and absorb oxygen from the air, thus becoming phosphates. When heated in a dry condition, they set free the hydride of P, and are converted into pyrophosphates; some also yield metallic phosphides.

Phosphorous Acid—H_3PO_3—is formed at the same time with phosphoric acid in the slow oxidation of P in the air. The decomposition of the trichloride by water gives it more conveniently:—

$$PCl_3 + 3H_2O = PO_3H_3 + 3HCl.$$

By evaporating this solution under the air-pump the phosphorous acid becomes crystalline. The crystals are readily soluble in water, and deliquesce in the air. It fuses at 70°, and decomposes on further heating into PH_3 and phosphoric acid:—

$$4PO_3H_3 = PH_3 + 3PO_4H_3.$$

In the air the acid absorbs oxygen, and changes to phosphoric acid. Hence, it is a strong reducing agent, and precipitates the free metals from many of their solutions. In the presence of water the halogens oxidize it to phosphoric acid.

It is a dibasic acid, forming two series of salts, in which 1 and 2 atoms* of H are replaced by metals. In the air, the phosphites do not oxidize, except under the influence of oxidizing agents. When heated, they generally decompose into hydrogen and pyrophosphates.

Phosphorous Oxide—P_2O_3 or P_4O_6—is formed when phosphorus is burnt in a rapid current of air. It consists of feathery crystals, which melt at 22.5° to a clear, colorless, mobile liquid. It boils without decomposition at 173.1° in an atmosphere of nitrogen or carbon dioxide. Its density equals 7.7, corresponding to the formula P_4O_6. In this respect it is analogous to arsenious and antimonious oxides. It is stable up to about 200°. On long standing with water it slowly dissolves, and the resulting solution yields all the reactions characteristic of phosphorous acid (*Jr. Chem. Soc.*, 57, 545).

Phosphoric Acid—PO_4H_3—or *Orthophosphoric acid*, is produced when the pentoxide is dissolved in hot water, and by the decomposition of the penta- or oxy-chloride ($POCl_3$) by water (see

---

* Therefore, the structural formula, $HPO(OH)_2$ is assigned to this acid. There appears to exist another phosphorous acid, at least in compounds, to which the formula $P(OH)_3$ belongs.

p. 142). It may be obtained by decomposing bone ash, $(PO_4)_2Ca_3$, with sulphuric acid, or, better, by oxidizing yellow phosphorus with nitric acid. The aqueous solution is evaporated to dryness in a platinum dish. The anhydrous acid consists of colorless, hard, prismatic crystals, which in the air deliquesce to a thick, acid liquid. Phosphoric acid is tribasic, forming three series of salts, called *acid* (PO_4H_2K), *neutral* (PO_4HK_2), and *basic* (PO_4K_3). As this designation does not entirely correspond with the behavior of the salts to litmus, it is more rational to term them *primary*, *secondary*, and *tertiary;* or to speak of them according to the number of hydrogen atoms replaced by metals, as, *e. g.*, monopotassium phosphate (H_2KPO_4), dipotassium (K_2HPO_4) phosphate, and tripotassium (K_3PO_4) phosphate.

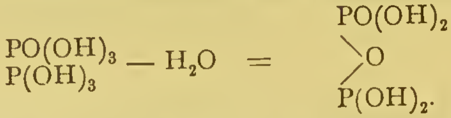
The tertiary phosphates, excepting the salts of the alkalies, are insoluble in water. With a silver nitrate $(AgNO_3)$ solution, soluble phosphates give a *yellow* precipitate of tri-silver phosphate, PO_4Ag_3.

Pyrophosphoric Acid—$H_4P_2O_7$—(structure, p. 218) is formed by the continuous heating of orthophosphoric acid to 200°–300°, until a portion of it dissolved in ammonium hydroxide does not yield a yellow but pure white precipitate with silver nitrate. The sodium salt is easily obtained by heating di-sodium phosphate:—

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O.$$

The acid presents a white crystalline appearance, and is readily soluble in water. When in solution, it slowly takes up water at ordinary temperatures, more rapidly when heated, and, like all anhydrides, passes into the corresponding acid—orthophosphoric acid. It is tetrabasic. Its salts are very stable, and are not altered by boiling with water; warmed with acids, they become salts of the ortho-acid. The soluble salts yield a *white* precipitate, $Ag_4P_2O_7$, with silver nitrate.

Hypophosphoric Acid—$P_2O_6H_4$.—While pyrophosphoric acid is an anhydride acid of phosphoric acid (p. 217), the so-called hypophosphoric may be viewed as a mixed anhydride of phosphoric and symmetrical phosphorous acids:—



$$\begin{matrix} PO(OH)_3 \\ P(OH)_3 \end{matrix} - H_2O = \begin{matrix} PO(OH)_2 \\ \rangle O \\ P(OH)_2. \end{matrix}$$

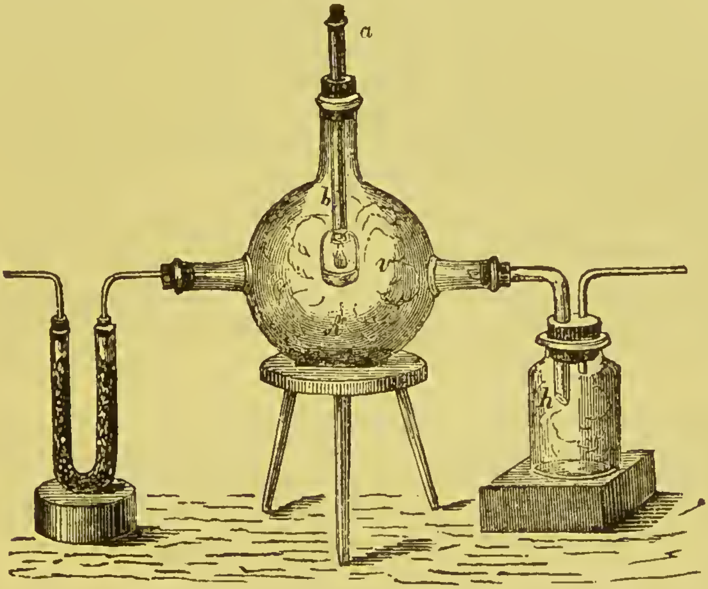
It is produced together with phosphorous and phosphoric acids, by the slow oxidation of moist phosphorus in the air. It is separated from these acids by means of its difficultly soluble sodium salt, $P_2O_6Na_2H_2 + 6H_2O$; by precipitating the solution of the latter with a soluble lead salt we get insoluble $P_2O_6Pb_2$. Its silver salt is more easily obtained by oxidizing phosphorus in the presence of silver nitrate. The free acid from the lead or silver salt is rather stable in a dilute solution, and below 30° may be concentrated to a syrup. At higher temperatures, more readily in the presence of hydrochloric or sulphuric acid, the acid decomposes into phosphoric and phosphorous acids. It is not a reducing agent, but is oxidized by potassium permanganate to phosphoric acid.

Metaphosphoric Acid—HPO_3 or PO_2OH—results upon heating the ortho- or pyro-acid to 400°. It can be more conveniently obtained by dissolving the pentoxide in cold water:—

$$P_2O_5 + H_2O = 2HPO_3.$$

It is a glassy, transparent mass (*Acidum phosphoricum glaciale*), which fuses on heating, and volatilizes at higher temperatures, without suffering any change. It deliquesces in the air, and dissolves with ease in water. (The commercial glassy phosphoric acid contains sodium and magnesium phosphate, and dissolves with difficulty in water). The solution coagulates albumen; this is a characteristic method of distinguishing the meta- from the ortho- and pyro-acids. In aqueous solution, the acid changes gradually, by boiling rapidly, into the ortho-acid:—

FIG. 86.



$$HPO_3 + H_2O = H_3PO_4.$$

It is a monobasic acid. Its salts, the metaphosphates, are readily obtained by the ignition of the primary salts of the ortho-acid:—

$$NaH_2PO_4 = NaPO_3 + H_2O.$$

When the aqueous solutions of these salts are boiled, they are converted into the ortho-primary salts. With silver nitrate the soluble *metaphosphates* give a *white* precipitate, $AgPO_3$.

In addition to the ordinary salts of metaphosphoric acid, various modifications of the same exist; these are derived from the polymeric meta-acids, $H_2P_2O_6$, $H_3P_3O_9$, $H_4P_4O_{12}$, etc. These acids arise from the corresponding polyphosphoric acids, which are obtained by the union of *n* molecules of the ortho-acid, with the separation of $n - 1$ molecules of water (p. 197), just as the meta-acid is formed from the ortho-. They are all changed to primary ortho-phosphates by boiling their solutions.

Phosphorus Pentoxide—P_2O_5, or *Phosphoric anhydride*—is obtained by burning phosphorus in a current of oxygen or dry air.

The following procedure serves for the preparation of it (Fig. 86): A piece of P, placed in an iron dish attached to the glass tube *a b*, is burned in the glass balloon *A*. The necessary amount of air is drawn through the vessel by means of an aspirator. It is first passed through the bent tube containing pieces of pumice-stone, moistened with sulphuric acid, in order to dry it perfectly. After the phosphorus has been consumed, fresh pieces of it are introduced into the little dish through *a b*, and the upper end of the tube closed with a cork. The P_2O_5 formed collects partly in *A* and partly in the receiver.

Phosphorus pentoxide is a white, voluminous, flocculent mass. It attracts moisture energetically and deliquesces in the air. It dissolves in cold water with hissing and yields metaphosphoric acid. Owing to its great affinity for water it serves as an agent for drying gases, and also for the withdrawal of water from many substances.

Chlor-Anhydrides of the Acids of Phosphorus.—The halogen derivatives of P, considered on page 140, may be viewed as the halogen anhydrides of phosphorous and phosphoric acids (p. 199). The compounds PCl_3, PBr_3, and PI_3, are derived from phosphorous acid, because they yield the latter acid with water:—

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

The compounds $POCl_3$, $POBr_3$, are the halogen anhydrides of phosphoric acid:—

$$POCl_3 + 3H_2O = PO(OH)_3 + 3HCl;$$

while PCl_5 and PBr_5 correspond to the normal hydroxide, $P(OH)_5$, which has not been obtained in a free condition.

The compound $PSCl_3$ is analogous to the oxychloride $POCl_3$. It is obtained by the action of PCl_5 upon hydrogen sulphide and some metallic sulphides:—

$$PCl_5 + H_2S = PSCl_3 + 2HCl.$$

This reaction is very similar to that occurring in the formation of phosphorus oxychloride. *Phosphorus sulphochloride*—$PSCl_3$—is a colorless liquid, fuming in the air and boiling at 124°. Water decomposes it into phosphoric and hydrochloric acids and hydrogen sulphide.

COMPOUNDS OF PHOSPHORUS WITH SULPHUR.

With sulphur, phosphorus affords a number of compounds which are obtained by direct fusion of P with S. As the union of ordinary P with S usually occurs with violent explosion, red phosphorus should be employed in preparing these compounds.

The compounds P_2S_3 and P_2S_5, analogous in constitution to P_2O_3 and P_2O_5, are solid crystalline substances, melting at higher temperatures and subliming without decomposition; P_2S_5 boils at 518°. Water changes them to hydrogen sulphide and the corresponding acids, phosphorous and phosphoric. They combine with metallic sulphides to form compounds (*e.g.*, PS_4K_3) which possess a constitution analogous to that of the salts of phosphoric acid (see sulpho-salts of arsenic).

At ordinary temperatures, P_2S and P_4S are liquids, which inflame readily in the air.

Besides the preceding, we have other phosphorus derivatives which contain N. These have been little studied, and at present offer little interest. Such compounds are PN_2H (phospham), PNO, $PNCl_2$. The so-called amid derivatives, $POCl_2NH_2$, $POCl(NH_2)_2$ and $PO(NH_2)_3$ are produced by allowing ammonia to act upon $POCl_3$. In these chlorine is replaced by the amido-group NH_2.

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3. OXYGEN DERIVATIVES OF ARSENIC.

As_2O_3 Arsenic trioxide.	AsO_3H_3 Arsenious acid.
As_2O_5 Arsenic pentoxide.	AsO_4H_3 Arsenic acid.

Arsenic Trioxide, As_2O_3, or *Arsenious anhydride*, occurs in nature as arsenic "bloom." It is produced by the burning of arsenic in oxygen or in the air, and by the oxidation of the metal with dilute nitric acid. It is obtained metallurgically on a large scale as a by-product in the roasting of ores containing arsenic. The trioxide thus formed volatilizes and is collected in walled chambers, in which it condenses in the form of a white powder (white arsenic, poison flour). To render it pure, it is again sublimed in iron cylinders, and obtained in the form of a transparent, amorphous glassy mass (arsenic glass), the specific gravity of which equals 3.78. Upon preservation, this variety gradually becomes non-transparent and porcelaneous, acquires a crystalline structure, and its specific gravity decreases to 3.69. Upon dissolving this oxide in hot hydrochloric acid, it crystallizes, on cooling, in shining, regular octahedra. At the same time the interesting phenomenon is observed, that when the solution of the glassy variety crystallizes it phosphoresces strongly in the dark, while the porcelaneous does not exhibit this property. Arsenic trioxide crystallizes in similar forms of the regular system when its vapors are rapidly cooled, but upon cooling slowly, it assumes the shape of rhombic prisms; therefore, it is dimorphous. When heated in the air, it sublimes above 218°, without fusing; upon higher pressure, however (in sealed tubes), it melts to a liquid which solidifies to a glassy mass.

The vapors of As_2O_3 have the vapor density 198 ($H = 1$), which continues constant to 1560°. Corresponding to formula As_2O_3 ($= 198$), the vapor density should be $\frac{198}{2} = 99$. The vapor density determined experimentally is just twice as great, therefore the gas molecules of the trioxide possess the double formula As_4O_6. We have already noticed that the molecule of free arsenic consists of four atoms (As_4): this complex arsenic group, consequently, is retained in the trioxide; while in arsine (AsH_3) and arsenious chloride ($AsCl_3$) the molecules contain but 1 atom of arsenic.

The trioxide dissolves with difficulty in water; the solution possesses a sweetish, unpleasant metallic taste, exhibits but feeble acid reaction, and is extremely poisonous. The oxide is very soluble in acids, and probably forms salts with them; at least, on boiling a solution of As_2O_3 in strong hydrochloric acid, arsenious chloride, $AsCl_3$, volatilizes. From this and its feeble acid nature we perceive an indication of the basic character of the trioxide corresponding to the already partially metallic nature of arsenic (see p. 150).

Nascent hydrogen converts the trioxide into arsine (AsH_3); but when heated with charcoal it is reduced to the metallic state. Upon heating As_2O_3 in a narrow glass tube with C, the reduced arsenic deposits as a metallic mirror on the sides. Oxidizing agents convert it into arsenic acid.

Arsenious Acid—H_3AsO_3, corresponding to As_2O_3, is not known in a free condition. It probably exists in the aqueous solution, but the anhydride separates out upon evaporation. In its salts (*arsenites*) it is tribasic and usually affords tertiary derivatives:—

$$Ag_3AsO_3, \; Mg_3(AsO_3)_2.$$

The alkali salts, soluble in water, absorb oxygen from the air and serve as powerful reducing agents, they themselves becoming arseniates.

Other salts exist which are derived from the meta-arsenious acid, $HAsO_2$ (p. 205).

Arsenic Acid—H_3AsO_4—is obtained by the oxidation of arsenic or its trioxide with concentrated nitric acid or by means of chlorine. Upon evaporating the solution rhombic crystals of the formula $H_3AsO_4 + \frac{1}{2}H_2O$ separate out; these deliquesce on exposure. They melt at 100°, lose their water of crystallization and yield orthoarsenic acid H_3AsO_4, which heated to 140–180° passes into *pyroarsenic acid*—$H_4As_2O_7$:—

$$2H_3AsO_4 = As_2O_7H_4 + H_2O.$$

At 200° this again loses water and becomes *Meta-arsenic acid*—$HAsO_3$. With water the last two acids become ortho- again; hence the latter is perfectly analogous to phosphoric acid.

At a red heat the meta-arsenic acid loses all its water and becomes *Arsenic Pentoxide*—As_2O_5, a white, glassy mass. Very strong ignition breaks this up into As_2O_3 and O_2; in contact with water it gradually changes to arsenic acid.

Orthoarsenic acid is readily soluble, and is a strong tribasic acid. Its salts—the arseniates—are very similar to the phosphates and are isomorphous with them. With the soluble salts silver nitrate gives a reddish-brown precipitate of tri-silver-arseniate, Ag_3AsO_4.

COMPOUNDS OF ARSENIC WITH SULPHUR.

Like phosphorus, arsenic, upon fusion with sulphur, yields several compounds. The metallic nature of arsenic is seen in these derivatives, because they, according to the common method of forming the metallic sulphides, can be obtained by the action of hydrogen sulphide upon the oxygen derivatives of arsenic:—

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O.$$

Arsenic Trisulphide—As_2S_3—is precipitated from solutions of arsenious acid or its salts by hydrogen sulphide, as a lemon-yellow amorphous powder. It may also be obtained from arsenic acid solutions, but then it contains admixed S, as the acid is first reduced to arsenious acid and then precipitated:—

$$As_2O_5 + 2H_2S = As_2O_3 + 2H_2O + 2S.$$

This compound is most readily prepared by fusing As_2O_3 with sulphur. It occurs as *auripigment* in nature in the form of a brilliant, leafy, crystalline mass of gold-yellow color, and the specific gravity 3.4. On fusing artificially prepared arsenic trisulphide it solidifies to a similar yellow mass, the specific gravity of which equals, however, 2.7. In water and acids the trisulphide is insoluble, but dissolves readily in ammonium hydroxide and the alkalies.

Arsenic Pentasulphide—As_2S_5—separates as a bright yellow powder from the solution of sodium sulpharseniate, Na_3AsS_4 (see below), upon the addition of acids.

The **Arsenic Disulphide**—As_2S_2—also exists. It occurs in nature as *Realgar*, forming beautiful, ruby-red crystals, of specific gravity 3.5. It is applied as a pigment. It is prepared artificially by fusing As with S.

Arsenic Sulpho-Salts.—Owing to the similarity of sulphur to oxygen we may anticipate for arsenic (as also for other elements) the existence of sulphur acids corresponding to the oxygen acids, *e.g.*, sulpharsenious acid, H_3AsS_3, and sulpharsenic acid, H_3AsS_4. However, these acids are unknown in a free state, although their salts, known as *sulphur-* or *sulpho-salts*, are found, and they correspond perfectly with the oxygen salts. Just as the latter arise by the union of metallic oxides with acid oxides, so the sulpho-salts are formed by the combination of alkaline sulphides with those sulphur derivatives corresponding to the acid oxides (acid sulphides) :—

$$As_2S_3 + 3K_2S = \underset{\text{Tripotassium sulpharsenite.}}{2K_3AsS_3}$$

$$As_2S_5 + 3K_2S = \underset{\text{Tripotassium sulpharseniate.}}{2K_3AsS_4}$$

For the preparation of these sulpho-salts, arsenic sulphide is dissolved in the aqueous solution of potassium or sodium sulphide, or hydrogen sulphide is conducted through the alkaline solution of the oxygen salts :—

$$K_3AsO_4 + 4H_2S = K_3AsS_4 + 4H_2O.$$

The sulpho-salts or the alkalies and ammonium are easily soluble in water, and when the solution is evaporated they generally separate in crystals. Acids decompose them, arsenic sulphide separating out and hydrogen sulphide becoming free :—

$$2K_3AsS_4 + 6HCl = As_2S_5 + 6KCl + 3H_2S.$$

Antimony, carbon, tin, gold, platinum and some other metals form sulpho-salts similar to those of arsenic (and of phosphorus).

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4. OXYGEN COMPOUNDS OF ANTIMONY.

The oxygen derivatives of antimony are analogous in constitution to those of arsenic: Sb_2O_3 and Sb_2O_5. The metallic nature of antimony, which we observed appearing in the halogen derivatives, shows itself quite distinctly here. The lowest oxygen compound does not possess acid, but basic properties almost solely ; it forms salts with acids only, hence is called *Antimony oxide*. The normal hydrate H_3SbO_3, corresponding to arsenious acid, H_3AsO_3, is not known. A hydrate, SbO_2H or $SbO.OH$, analogous to meta-arsenious acid, does exist ; it deports itself like a base.

The higher oxidation product, the pentoxide, Sb_2O_5, on the contrary, has an acid nature and yields salts with the bases. The hydrate, SbO_4H_3, or ortho-antimonic acid, and its salts, have not been obtained. The known salts are derived from pyro-antimonic acid, $H_4Sb_2O_7$, and meta-antimonic acid, $HSbO_3$; these exist in a free condition.

Antimony Oxide—Sb_2O_3 or Sb_4O_6—is obtained by burning the metal in the air, or by oxidizing it with dilute HNO_3. By sublimation it may be obtained in two different crystal systems, in regular octahedra and in rhombic prisms. Arsenic trioxide also crystallizes in the same forms; therefore the two compounds are isomorphous. On adding sodium carbonate to the solution of the trichloride a white precipitate of antimony hydrate or antimonious acid, $HSbO_2$, separates out:—

$$2SbCl_3 + 3Na_2CO_3 + H_2O = 2SbO.OH + 6NaCl + 3CO_2.$$

The hydrate is changed to oxide by boiling. The latter and the hydrate dissolve in sodium and potassium hydroxide, and, very probably, form salts ($NaSbO_2$) which decompose upon evaporating the solution. In this behavior the acid nature of antimony hydrate is also seen; therefore it has received the name of antimonious acid.

The oxide forms salts with acids, which are derived either from the normal hydrate, H_3SbO_3, or from the hydrate, $HSbO_2 = SbO.OH$. In the salts of the first kind we have 3 hydrogen atoms of the hydrate replaced by acid radicals, or, what is the same, a trivalent antimony atom displacing 3 hydrogen atoms of the acids:—

$$SbO_3(NO_2)_3 \text{ or } (NO_3)_3Sb.$$

Antimony nitrate.

In the second variety of antimony salts derived from the hydrate, SbO.OH, hydrogen is replaced by a monovalent acid residue, or the hydrogen of the acid is substituted by the monovalent group, SbO, known as *antimonyl*:—

$$SbO.O.NO_2 \text{ or } NO_3.SbO.$$

Antimonyl nitrate.

Of these salts may be mentioned the following:—

Antimony Sulphate—$(SO_4)_3Sb_2$—which separates when a solution of the oxide in sulphuric acid is cooled.

Antimonyl Sulphate—$SO_4(SbO)_2$—is formed when antimony oxide is dissolved in somewhat dilute sulphuric acid, and crystallizes in fine needles on cooling. Water decomposes both, forming basic salts; hence the basic nature of antimony oxide is slight.

Antimonic Acid—$HSbO_3$—or, more correctly, *Meta-antimonic acid*, is obtained upon warming antimony with concentrated nitric acid, and is a white powder, almost insoluble in water and in nitric acid, but reddens blue litmus paper. It is a weak monobasic acid, the salts of which are mostly insoluble.

If antimony pentachloride be mixed with much water, **Pyroantimonic Acid**, $H_4Sb_2O_7$, separates as a white powder. Its salts are produced by fusing antimonic acid or meta-antimoniates with potassium or sodium hydroxides:—

$$2KSbO_3 + 2KOH = K_4Sb_2O_7 + H_2O.$$

Hydrochloric acid precipitates pyroantimonic acid from the solutions of these salts.

By gentle ignition the meta- and pyro-acids yield **Antimony Pentoxide,** Sb_2O_5, a yellow, amorphous mass, soluble in hydrochloric acid. By heating the oxygen compounds for some time with air access they are converted into the oxide, Sb_2O_4, which can be viewed as antimonyl antimoniate ($SbO_3.SbO$), or as a mixed anhydride $\left.\begin{matrix}SbO_2\\SbO\end{matrix}\right\}O$. It is a white powder, becoming yellow when heated, and is non-volatile.

COMPOUNDS OF ANTIMONY WITH SULPHUR.

These are perfectly analogous to the S compounds of arsenic, and form sulphosalts with alkaline sulphides, corresponding to the oxygen salts. Acids precipitate antimony sulphide from the sulphosalts.

Antimony Trisulphide—Sb_2S_3—is found in nature as stibnite, in radiating crystalline masses of dark-gray color and metallic lustre; specific gravity = 4.7. When heated it melts and sublimes. The artificial sulphide obtained by precipitating a solution of the oxide with hydrogen sulphide, is an amorphous red powder. When fused, it solidifies to a mass exactly like stibnite. The sulphide dissolves in concentrated HCl, upon warming, to form antimony trichloride.

The compound, Sb_2S_2O, occurring in nature as red stibnite, can be artificially prepared, and serves as a beautiful red color, under the name of *antimony cinnabar.* *Kermes minerale,* employed in medicine, is obtained by boiling antimony sulphide with a sodium carbonate solution, and is a mixture of Sb_2S_3 and Sb_2O_3.

Antimony Pentasulphide—Sb_2S_5—or gold sulphur (*sulphur auratum*) is precipitated by H_2S from acid solutions of antimonic acid; it is more conveniently obtained by the precipitation of sodium sulphantimoniate, Na_3SbS_4, with hydrochloric acid:—

$$2Na_3SbS_4 + 6HCl = Sb_2S_5 + 6NaCl + 3H_2S.$$

It is an orange-red powder, like the trisulphide; it decomposes on being heated into Sb_2S_3 and S_2. It dissolves to antimony trichloride in strong hydrochloric acid, with separation of sulphur and hydrogen sulphide.

Sodium Sulphantimoniate—Na_3SbS_4 (Schlippe's salt), results from boiling pulverized Sb_2S_3 with sulphur and sodium hydroxide. Upon concentrating the solution it crystallizes in large yellow tetrahedra, containing 9 molecules of H_2O ($SbS_4Na_3 + 9H_2O$); exposed to the air it becomes covered with a brown layer of Sb_2S_5. It serves principally for the preparation of the officinal gold sulphur.

The affinity of the elements of the nitrogen group for hydrogen diminishes with increase of atomic weight, and corresponds to the addition of metallic character, while the affinity for chlorine, concluded from the thermo-chemical relations, generally increases (compare p. 150). However, the heat disengagement in the formation of $AsCl_3$ is somewhat less than that in the case of PCl_3, which would afford a partial explanation for the non-existence of the compounds AsX_5 (see p. 146). The slight affinity of arsenic is seen more distinctly in the oxygen compounds, because, as in the case of the halogen and oxygen groups (pp. 186 and 204), the arsenic corresponding to bromine and selenium—

$$Br = 79.96 \qquad Se = 79.1 \qquad As = 75,$$

shows a less heat disengagement in the formation of its compounds:—

$(N,O_4,H_3,Aq.) = 117.4$ $\qquad$ $(N_2,O_5,Aq.) = 29.8$
$(P,O_4,H_3,Aq.) = 305.3$ $\qquad$ $(P_2,O_5) = 363.8$
$(As,O_4,H_3,Aq.) = 215.2$ $\qquad$ $(As_2,O_5) = 219.4$

Phosphoric acid is, therefore, more stable and more energetic than nitric and arsenic acids; nitric acid oxidizes phosphorus and arsenic to phosphoric and arsenic acids. The latter acid is readily reduced to arsenious acid.

VANADIUM.	NIOBIUM.	TANTALUM.
Vd = 51.2	Nb = 94.2	Ta = 183

The three rare elements, vanadium, niobium and tantalum, are closely related to the Phosphorus group. They yield derivatives very much like those of P; but possess a more metallic character, and do not combine with hydrogen. They exhibit many characteristics similar to those of chromium, iron and tungsten, with which they are frequently associated in their naturally occurring compounds (compare the Periodic System of the elements).

Vanadium occurs in nature principally in the form of salts of vanadic acid (vanadium lead ore) and in some iron ores. It may be obtained free by igniting its chlorides in a current of hydrogen. It is a grayish-white, metallic, lustrous powder, of specific gravity 5.5. It is difficultly fusible, and does not change in the air. When heated, it burns to Vd_2O_5.

Vanadium Trichloride—$VdCl_3$—forms red plates, which readily deliquesce in the air; it is not volatile.

Vanadium Oxychloride—$VdOCl_3$—results on heating a mixture of Vd_2O_3 and C in chlorine gas. It is a lemon-yellow liquid, of specific gravity 1.84, and boils at 120°. It fumes strongly in the air and decomposes with water (analogous to phosphorus oxychloride) into vanadic acid and hydrochloric acid. Its vapor density equals 86 ($VdOCl_3 = 173.2$).

Vanadium Oxide—Vd_2O_3—is a black powder obtained by heating Vd_2O_5 in hydrogen. It combines with O, to form Vd_2O_5.

Vanadium Pentoxide—Vd_2O_5—or vanadic anhydride, is a brown mass obtained by fusing the naturally occurring vanadates with nitre, etc. It is soluble in the alkalies, and forms salts of *Vanadic*, H_2VdO_4, and *Metavanadic* acids, $HVdO_3$, with the metals. All these compounds are similar in constitution to those of P. In addition to these, vanadium forms other compounds, constituted like those of sulphur and chromium. In this class belong $VdCl_2$ (dichloride), the tetrachloride, $VdCl_4$, vanadious oxide, VdO, vanadium dioxide, VdO_2, and $VdOCl_2$. The tetrachloride, $VdCl_4$, is a red-brown liquid, boiling at 154°; its vapor density equals 96 ($VdCl_4 = 191.6$). Niobium and tantalum are not known in a free state. The chlorides, $NbCl_5$ and $TaCl_5$, are volatile and are decomposed by water. Niobium and tantalum unite with potassium fluoride, forming double salts, *e. g.*, $2KFl.NbFl_5$ and $2KFl.TaFl_5$; also $2KFl.NbOFl_3$ and $2KFl.TaOFl_3$. When potassium niobium fluoride, $2KFl.NbFl_5$, is heated with sodium, *niobium hydride* is formed. This is a grayish-black powder. If it is heated it burns to niobic anhydride, Nb_2O_5, and water. The oxides, Nb_2O_5, and Ta_2O_5, form salts of niobic (H_3NbO_4) and tantalic (H_3TaO_4) acids with bases.

OXYGEN DERIVATIVES OF THE ELEMENTS OF THE CARBON GROUP.

Because of the analogy with the hydroxyl derivatives of the elements of the first three groups, $ClO_3.OH$, $SO_2(OH)_2$, $PO(OH)_3$, we may assume the existence of the following normal hydroxides, corresponding to the halogen derivatives, CCl_4, $SiCl_4$, $GeCl_4$, and $SnCl_4$, for the tetravalent elements—carbon, silicon, germanium, and tin:—

$\overset{\text{IV}}{\text{C}}(OH)_4$,	$\overset{\text{IV}}{\text{Si}}(OH)_4$,	$\overset{\text{IV}}{\text{Ge}}(OH)_4$.
Normal Carbonic acid.	Normal Silicic acid.	Normal Germanic acid.

These normal hydrates or acids have but little stability, and mostly exist only in some derivatives. By the separation of a molecule of water, they pass into

	CO_3H_2	SiO_3H_2	GeO_3H_2
or			
	$\overset{\text{IV}}{\text{C}}O(OH)_2$ Carbonic acid.	$\overset{\text{IV}}{\text{Si}}O(OH)_2$ Silicic acid.	$\overset{\text{IV}}{\text{Ge}}O(OH)_2$. Germanic acid.

These hydroxyl derivatives deport themselves toward the normal just as the meta-acids of the elements of the N group do to the ortho-acids (see p. 204). They constitute the ordinary acids of the tetravalent elements, carbon, silicon, and tin, and as they contain 2 hydroxyl groups, are dibasic.

Carbon is the lowest member of this group, with the least atomic weight. Among the elements of the other three groups corresponding to it are: nitrogen, oxygen, and fluorine:—

$$C = 12, \quad N = 14.04, \quad O = 16, \quad Fl = 19.$$

Fluorine and oxygen do not afford any oxygen acids. The normal acids of nitrogen, $N(OH)_5$ and $NO(OH)_3$, are very unstable, and pass readily into the meta-acids, $NO_2.OH$ and $NO.OH$. The normal carbonic acid ($C(OH)_4$) corresponds to this, but is not capable of existing. Indeed, the meta- or ordinary carbonic acid, H_2CO_3, is also very unstable and at once decomposes, when separated from its salts, into water and carbon dioxide, CO_2. Even silicic, germanic, and stannic acids break up readily into water and their oxides:—

CO_2	SiO_2	SnO_2
Carbon dioxide.	Silicon dioxide.	Stannic oxide.

I. OXYGEN COMPOUNDS OF CARBON.

Carbon Dioxide—CO_2—or carbonic anhydride (generally called carbonic acid). It is produced when carbon or its compounds are burned in air or oxygen. It is found free in the air (in 100 volumes, upon average, 0.05 volumes CO_2), in many mineral springs (acid springs), and escapes in large quantities from the earth in many volcanic districts. It occurs in the liquid form, enclosed in the cavities of many crystalline minerals. It is prepared on a large scale by burning coke; in the laboratory it may be most conveniently obtained by the decomposition of calcium carbonate (marble or chalk) with dilute hydrochloric acid:—

$$\underset{\text{Calcium carbonate.}}{CaCO_3} + 2HCl = \underset{\text{Calcium chloride.}}{CaCl_2} + CO_2 + H_2O.$$

Carbon dioxide is a colorless gas, of sweetish odor and taste. Its gas density equals 1.527 (air = 1), or 22 (H = 1), corresponding to the molecular formula, $CO_2 = 44$. Owing to its weight, the gas may be collected by air displacement, and may be poured from one vessel into another filled with air. Faraday was the first to liquefy carbon dioxide by pressure. The apparatus of Thilorier and Natterer were employed to this end. At present liquid dioxide is brought into market enclosed in wrought-iron cylinders, and is applied quite regularly, *e. g.*, to compress cast steel. Carbon dioxide can only be liquefied below + 30.9°—this is its critical temperature (p. 47). Its tension (critical pressure) at this point equals 73.6 atmospheres. If liquid CO_2, enclosed in some suitable vessel, be allowed to escape into the air by opening a stop-cock (ordinary pressure), it immediately solidifies (see below) to a white, snowy mass. This is because in the evaporation of a part of the liquid so much heat is withdrawn that the remainder becomes solid. Solid carbon dioxide is a very poor conductor of heat and vaporizes very slowly. Notwithstanding its low temperature it can be handled without serious result, because it is always surrounded by a gaseous layer, and is, consequently, not in immediate contact with the skin. If, however, it be pressed between the fingers it will produce painful burns.

The temperature of the solid carbon dioxide vaporizing in the air under ordinary temperature is about—78° (below—99° according to Faraday). When the solid dioxide is mixed with a little ether it forms a paste, and then conducts heat better, and is, therefore, well adapted as a cooling agent. In vacuo its temperature diminishes to —140° C.

Liquid carbon dioxide is readily obtained by filling the snowy mass into a thick tube, and then sealing the latter. It is a colorless, very mobile liquid. Its sp. gr. is 0.923 at 0°, 0.868 at 10°, and 0.782 at 20°. Its coefficient of expansion is, consequently, greater than that of the gases. Other gases behave similarly, but only such as are condensed under great pressure. If liquid carbon dioxide, contained in a glass tube, be heated, it expands rapidly and suddenly passes, at the critical temperature + 30.9°, into gas. This behavior enables us to determine without difficulty whether the liquids contained (see above) in minerals are liquid carbon dioxide.

If liquid carbon dioxide, confined in a glass tube, be cooled by a mixture of solid, snowy dioxide and ether (see above), it will solidify to a transparent ice-like mass, which will fuse at —65°.

The tension of the solid or liquid dioxide, which at the same time indicates the pressure necessary for condensation at various temperatures, is given in the following table:—

Temperature.	Tension.	Temperature.	Tension.
+ 30.9°	73.6 atmos.	— 21°	21.5 atmos.
20°	56.0 "	— 40°	11.0 "
10°	45.0 "	— 59.4°	4.6 "
0°	38.5 "	— 70.6°	2.3 "
		— 78°	1.2 "

At the temperature of fusion of the solid dioxide (—65°) the tension equals about 3.5 atmospheres: the resulting liquid has this tension at this temperature. If the external pressure exerted upon it be less, it cannot exist as a liquid, but must immediately pass into the gaseous state. Herein we observe why the solid dioxide (under ordinary pressure) does not melt in the air, but vaporizes at once; and, further, it explains why the liquid dioxide, subjected to the ordinary atmospheric pressure, cannot continue in this state—why it either is gasified at once, or changed to the solid form.

Many other fusible solids behave like the dioxide. If the tension of their vapors at the fusion temperature exceeds that of the external atmospheric pressure they do not melt in the air, because the resulting liquid is immediately transformed into vapor; they vaporize (sublime) directly, without previous fusion. Such bodies are, *e. g.*, arsenic, arsenic trioxide, As_2O_3, camphor, hexachlorethane C_2Cl_6, etc. They can only be fused under increased pressure (in sealed tubes). Again, all solids fusible in the air (under ordinary pressure) may be converted directly into gases by removing the external pressure. Thus iodine fuses at 114°, but sublimes in a vacuum without previous fusion. Mercuric chloride fuses at 265°, but not if the external pressure be less than 420 mm. Water melts at 0°, its tension at this temperature is 4.6 mm. If the external pressure be less (in vacuo), it will no longer melt, but vaporize at once. The pressure below which solids no longer melt has been called the *critical pressure* (Carnelley). It is, of course, understood that this is nothing more than the tension of the substance at its point of fusion.

Water dissolves its volume of the gas at 14°; at 0° it takes up 1.79 vols. This proportion remains constant for every pressure, *i. e.*, at every pressure the same volume of gas is absorbed. As gases are condensed in proportion to the pressure, the quantity of absorbed gas is also proportional to the former. Hence 1 volume of H_2O absorbs, at 14° and two atmospheres, 2 volumes, at 3 atmospheres 3 volumes, etc., of carbon dioxide—measured at ordinary pressure. The gas absorbed at higher pressure escapes with effervescence of the liquid when the pressure is diminished; upon this depends the sparkling of soda water and champagne, which are saturated with CO_2 under high pressure. Every naturally occurring water, especially spring water, holds CO_2 in solution, which imparts to it a refreshing taste.

As the product of a complete combustion carbon dioxide is not combustible, and is unable to support the combustion of most bodies, a glimmering chip is immediately extinguished in it. In a similar manner it is non-respirable. Although it is not poisonous, in the true sense of the word, yet the admixture of a few per cent. of CO_2 to the air makes it suffocating, as it retards the separation of the same gas from the lungs.

It is decomposed by continued action of the electric sparks into carbonous oxide (CO) and oxygen; upon heating to 1300° it suffers a partial decomposition (dissociation) into CO and O. It is also decomposed when conducted over heated K or Na, with separation of carbon; the potassium combines with oxygen to form potassium oxide:—

$$CO_2 + 2K_2 = C + 2K_2O,$$

which forms potassium carbonate (K_2CO_3), with excess of CO_2. Glowing carbon reduces the dioxide to the monoxide (p. 235). CO is analogously formed on conducting a mixture of the dioxide and hydrogen (equal volumes) through a tube heated to redness:—

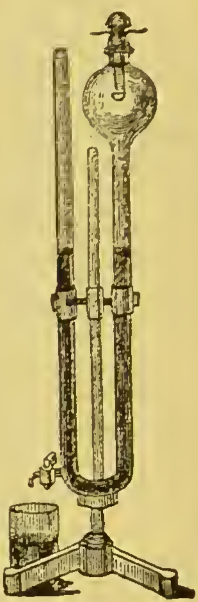
$$CO_2 + H_2 = CO + H_2O.$$

The composition of carbon dioxide is readily determined by burning a weighed quantity of pure carbon (diamond or graphite) in a current of oxygen, and ascertaining the weight of the resulting gas. From the formula CO_2 it follows that in one volume it contains an equal volume of O. We may satisfy ourselves of this by burning C in a definite volume of O; after cooling, there is obtained an equal volume of carbon dioxide:—

$$\underset{}{C} + \underset{\text{1 vol.}}{O_2} = \underset{\text{1 vol.}}{CO_2}.$$

The experiment is most practically executed by aid of the apparatus of Hofmann pictured in Fig. 87. The spherical-shaped expansion of the eudiometer limb of the **U** tube is closed by means of a glass stopper, through which two copper wires pass. The one wire bears a combustion spoon at its end, upon which lies the carbon to be burned, while the other wire terminates in a thin piece of platinum, which is in contact with the carbon. For the performance of the experiment, the air is expelled from the globe limb by means of a rapid current of oxygen, the stopper placed in air-tight, the mercury level noted, and the copper wires connected with the poles of an induction current from 3–4 Bunsen elements, which induces the burning of the carbon. As the volume of the enclosed gas is greatly expanded by the heat developed, it is advisable, in order to avoid the jumping out of the stopper, to previously reduce the pressure of the gas about two-thirds, by running out mercury. A practical modification of this apparatus consists in having the usual cylindrical eudiometer limb provided with two side tubes, in which carbon electrodes can be inserted. This same apparatus can also be employed for the illustration of the volume relations observed in the combustion of sulphur and other bodies.

FIG. 87.



The Physiological Importance of Carbon Dioxide.—The gas is present in the atmosphere, and is inhaled by the plants. The chlorophyl grains in the green parts of the plant decompose carbon dioxide in sunlight, with a partial separation of oxygen; by the mutal action of water and ammonia the innumerable carbon compounds peculiar to plants are formed from the residue. The respiration and life process of animals are essentially the reverse of the above. These absorb the oxygen of the air through the lungs; and, influenced by the blood corpuscles, it oxidizes the substances present in the blood, and in this manner shapes the life process. The final products of the oxidation are carbon dioxide and water, which are exhaled. The absorption of O by animals, and its separation by plants, as also the reverse course of CO_2, are about alike, so that the quantities of O and CO_2 in the air show no appreciable alteration.

In dry condition, carbon dioxide, like all anhydrides, exhibits neither basic nor acid reaction. In aqueous solution it colors blue litmus paper a faint red; upon drying the latter the red disappears, in consequence of the evaporation of the carbon dioxide.

We may then regard it as probable that free *carbonic acid*, H_2CO_3, is contained in the aqueous solution, but this readily decomposes into the dioxide, CO_2, and water. The salts of carbonic acid are produced by the action of carbon dioxide upon the bases:—

$$2KOH + CO_2 = \underset{\text{Potassium carbonate.}}{CO_3K_2} + H_2O.$$

Carbon dioxide is, therefore, easily absorbed by potassium and sodium hydroxide. On conducting it through a solution of calcium or barium hydroxide, a white precipitate of barium or calcium carbonate, $CaCO_3$, is produced.

Carbonic acid is dibasic, forming primary (acid) and secondary (neutral) salts, CO_3HK and CO_3K_2, called *carbonates*. As the acidity of carbonic acid is only slight, the secondary salts, obtained from strong bases, exhibit a basic reaction. Most acids expel the weak carbonic acid from its salts, with decomposition into carbon dioxide and water.

Carbon Monoxide—CO—is produced in the imperfect combustion of carbon by insufficient access of air, and when carbon dioxide is conducted over red-hot coals: $CO_2 + C = 2CO$. The forms of apparatus described, p. 234, serve for the demonstration of this volume relation. Carbon monoxide is, therefore, found in the generator gases produced by incomplete combustion.

Zinc dust reacts like carbon:—

$$CO_2 + Zn = ZnO + CO.$$

When carbon dioxide is conducted through a glass tube, containing zinc dust heated to a faint red heat, almost pure carbon monoxide escapes. A more convenient procedure consists in heating pulverized magnesium carbonate and zinc dust in a glass retort, when CO, containing CO_2, is eliminated; subsequently the former alone escapes. Pure monoxide is also formed upon heating zinc dust with chalk (in equivalent quantities): $Zn + CaCO_3 = ZnO + CaO + CO$.

The monoxide is produced, further, by igniting carbon with different metallic oxides, *e.g.*, zinc oxide: $ZnO + C = Zn + CO$. Water is similarly decomposed. On conducting aqueous vapor over burning carbon there is produced a mixture of carbon monoxide and hydrogen:—

$$C + H_2O = CO + H_2.$$

This gas mixture is known as *water gas*, and is applied technically. For preparation of carbon monoxide, oxalic acid is warmed with sulphuric acid: the latter withdraws water from the former, and the residue breaks up into carbon dioxide and monoxide:—

$$C_2O_4H_2 = CO_2 + CO + H_2O.$$

The disengaged mixture of gases is conducted through an aqueous solution of sodium hydroxide, by which the CO_2 is absorbed, the monoxide passing through unaltered. Pure monoxide may be prepared by heating yellow prussiate of potassium (see Iron) with 9 parts H_2SO_4. The resulting gas is conducted through sodium hydroxide to remove from it traces of CO_2 and SO_2. Its specific gravity equals 0.969 (air = 1) or 14 (H = 1), corresponding to the molecular formula CO = 28. It is one of the gases which are condensed with difficulty. Its critical temperature is −141° and its critical pressure is 35 atmospheres. Liquid carbon monoxide solidifies below 100 mm. pressure at —270°, and at 4 mm. pressure indicates a temperature of —220° (Olszewski). It is almost insoluble in water, but is readily dissolved by an ammoniacal solution of cuprous chloride (CuCl) with which it forms a crystalline compound, but this decomposes when its solution is heated and CO is again liberated. When ignited, it burns in the air, with a faintly luminous, beautiful blue flame, which distinguishes it from other combustible gases. With air or oxygen, it affords a very explosive mixture:—

$$\underset{\text{2 vols.}}{2CO} + \underset{\text{1 vol.}}{O_2} = \underset{\text{2 vols.}}{2CO_2}.$$

The union of carbon monoxide and oxygen takes place at very high temperatures; hence the burning flame of the gas is extinguished upon cooling. A flame or the spark from a powerful induction coil is necessary to ignite a *dry* mixture of carbon monoxide and oxygen. When the two gases are moist they are more easily ignited and combustible. This is explained by the fact that carbon monoxide unites with the aqueous vapor and yields the dioxide and hydrogen ($CO + H_2O = CO_2 + H_2$), which then combines with the oxygen and forms water (p. 102).

In consequence of its ready oxidation, it is capable of reducing most metallic oxides at a red heat:—

$$\underset{\text{(37.1 Cal.)}}{CuO} + \underset{\text{(28.5 Cal.)}}{CO} = Cu + \underset{\text{(96.9 Cal.)}}{CO_2} \ldots + (31.3 \text{ Cal.})$$

Some noble metals are precipitated from solutions of their salts by CO even in the cold. Thus, palladium is thrown out from its chloride solution, and a piece of paper moistened with palladious chloride is blackened by it (delicate test for CO).

As it easily oxidizes, carbon monoxide is reduced to carbon with difficulty. Burning bodies are extinguished by it. When it is heated with potassium it is decomposed with separation of carbon. When inhaled, it acts very poisonously, even in slight quantity, as it expels the oxygen of the blood. The carbon vapor, developed in heated ovens closed too soon, is carbon monoxide. As an unsaturated compound, this oxide, like ethylene, unites directly with

2 atoms of chlorine, to yield *carbon oxychloride*, or *phosgene gas*, $COCl_2$:—

$$\underset{\text{1 vol.}}{CO} + \underset{\text{1 vol.}}{Cl_2} = \underset{\text{1 vol.}}{COCl_2}.$$

This is obtained by bringing together equal volumes of CO and Cl_2 in direct sunlight, or, better, by conducting CO into $SbCl_5$. It is a colorless, suffocating gas, of specific gravity 49.4 (H = 1), agreeing with the molecular formula $COCl_2 = 98.9$. Water decomposes it into hydrogen chloride and carbon dioxide:—

$$COCl_2 + H_2O = CO_2 + 2HCl.$$

COMPOUNDS OF CARBON WITH SULPHUR.

Carbon Disulphide—CS_2—is formed, like the dioxide, by the direct union of carbon and sulphur; if vapors of the latter are led over ignited carbon the escaping disulphide vapors are condensed in a cooled receiver. It is a colorless, mobile liquid, of characteristic odor, solidifies at —116°, and refracts light strongly. Its specific gravity equals 1.29 at 0°. It is very volatile, boils at 47°, and burns with a blue flame, to carbon dioxide and sulphurous acid. When a mixture of carbon disulphide vapors and oxygen is ignited, a violent explosion ensues:—

$$\underset{\text{1 vol.}}{CS_2} + \underset{\text{3 vols.}}{3O_2} = \underset{\text{1 vol.}}{CO_2} + \underset{\text{2 vols.}}{2SO_2}.$$

In nitrous oxide, the vapors burn with a bright, blinding flame. On blowing a strong current of air upon carbon disulphide in a porcelain capsule (which conducts heat poorly), so much heat is absorbed by the evaporation, that the residual liquid solidifies to a white, snow-like mass. Carbon disulphide is insoluble in water; but mixes, in every proportion, with alcohol and ether. It dissolves iodine with a violet-red color, and serves as an excellent solvent for sulphur, phosphorus, caoutchouc, and the fatty oils. On conducting the CS_2 vapors over heated zinc dust, all the sulphur unites with the zinc, forming zinc sulphide, while the carbon separates as soot:—

$$\underset{(-\,12.6\ \text{Cal.})}{CS_2} + 2Zn = \underset{(2\,\times\,41.5\ \text{Cal.})}{2ZnS} + C\ .\ .\ . + (95.6\ \text{Cal.})$$

Most metals react in a similar manner.

Carbon disulphide may be viewed as the anhydride of *sulphocarbonic acid*—H_2CS_3. The salts of this acid are obtained by the solution of CS_2 in alkaline sulphides (see Sulpho-salts, p. 226):—

$$CS_2 + K_2S = K_2CS_3.$$

On adding hydrochloric acid to the solutions of these salts the sulphocarbonic acid separates as a reddish-brown oil. This decomposes readily.

The sulphur compound corresponding to CO is not known:* there exists, however, one containing both oxygen and sulphur—**Carbon oxysulphide, COS.** It is produced (in small quantity) when a mixture of sulphur vapors and carbon monoxide gas is passed through red-hot tubes and by heating carbon disulphide with sulphuric oxide:—

$$CS_2 + 3SO_3 = COS + 4SO_2.$$

It is most readily obtained from potassium sulphocyanide—CN.SK (see Organic Chemistry) by the action of dilute sulphuric acid. It is a colorless gas, with an odor reminding one of carbon dioxide and hydrogen sulphide. It is present in some sulphur springs. It is very readily inflammable and burns with a blue flame:—

$$\underset{\text{2 vols.}}{2COS} + \underset{\text{3 vols.}}{3O_2} = \underset{\text{2 vols.}}{2CO_2} + \underset{\text{2 vols.}}{2SO_2}.$$

It is decomposed at a red heat into CO and sulphur. It is soluble in an equal volume of water, decomposing gradually into the dioxide and hydrogen sulphide:—

$$COS + H_2O = CO_2 + SH_2.$$

CYANOGEN COMPOUNDS.

Of the innumerable compounds of C treated in organic chemistry, we will here mention only those of cyanogen, as they are of importance in inorganic chemistry.

Nitrogenous carbon compounds heated with potassium hydroxide yield potassium cyanide—CNK—which with iron forms the so-called yellow prussiate of potassium, $K_4Fe(CN)_6$. All the other cyanogen derivatives may be prepared from these two compounds. They all contain the group CN, called *cyanogen*. In it we have a trivalent nitrogen atom combined with a tetravalent carbon atom; the fourth affinity of the latter is not saturated: $\overset{III}{N}\equiv\overset{IV}{C}-$: it is similar, therefore, to the groups OH, NH_2, CH_3, and is a monovalent radical. In chemical behavior the cyanogen group is very similar to the halogens chlorine and bromine; with the metals it forms metallic cyanides (KCN, AgCN) very similar to the haloid salts. Hydrogen cyanide is evolved when the cyanides are heated with sulphuric acid:—

$$2KCN + H_2SO_4 = K_2SO_4 + 2HCN.$$

Hydrogen Cyanide, HCN, is a colorless, mobile liquid, of peculiar odor, and boiling at 27°. It is an acid, forming salts with metals and bases, and is known as *Hydrocyanic or Prussic*

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* Upon standing in sunlight CS_2 is said to break up into S and CS—a chestnut-brown powder of specific gravity 1.66.

acid. Both it and its salts are very powerful poisons. If the CN group is separated from its salts it doubles itself, yielding *dicyanogen* or *free cyanogen*, C_2N_2 ($N \equiv C - C \equiv N$), because, like the other monovalent groups (as CH_3, see p. 172), it cannot exist in a free condition.

The heat occurring in the formation of the simplest carbon compounds (from amorphous carbon) above cited corresponds with the symbols :—

$(C,O) = 28.5.$ $(CO,O) = 68.3.$ $(C,O_2) = 96.9.$
$(C,O,S) = 1.4.$ $(C,S_2) = -12.6.$ $(C,N,H) = -28.3.$
$(CO,Cl_2) = 4\ 3.$ $(CO_2,Aq.) = 5.8.$

If an element combine with another according to multiple proportions, there usually occurs, in the union of the first atom, a greater disengagement of heat than with the following atom (compare nitrogen oxides, p. 216). The numbers above, on the contrary, show that the union of the second atom of oxygen with carbon (CO,O) sets free 68.3 calories; that of the first atom (C,O), however, only 28.5 calories. This can only be explained by the fact that, for the vaporization and disaggregation of the solid carbon molecules, heat is necessary. If we assume that the direct union of the first atom, also disengaged 68.3 calories, it would follow from this that, in the dissociation of 12 parts carbon by weight into gaseous free atoms, 39.7 (= 68.3 — 28.5) calories were absorbed. This would explain the heat absorption in the production of CS_2, CNH, C_2H_2, while otherwise heat is invariably disengaged in every direct chemical union.

Comparing the elements of the carbon group with each other, we discover that the heat disengagement is greatest with the compounds of silicon :—

$(C,Cl_4) = 28.3.$ $(Si,Cl_4) = 157.6.$ $(Sn,Cl_4) = 129.2.$
$(C,O_2) = 96.9.$ $(Si,O_2) = 219.0.$ $(Sn,O_2,H_2O) = 133.5.$

From these numbers we observe that tin dioxide, but not that of silicon, can be reduced by carbon.

2. OXYGEN COMPOUNDS OF SILICON.

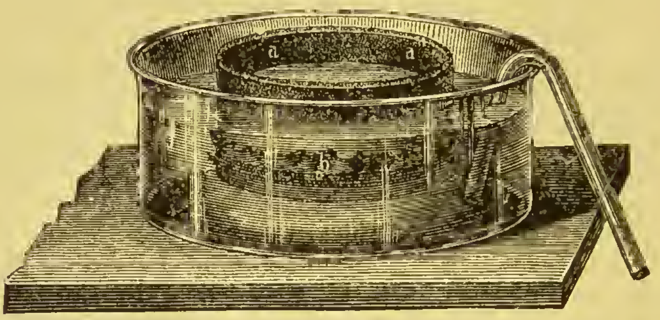
Silicon Dioxide, SiO_2 (*Silica*), is widely distributed in nature as rock crystal, quartz, sand, etc. It is artificially obtained as a white, amorphous powder, of specific gravity 2.2, by the combustion of amorphous silicon, or by the ignition of the silicic acids. It only occurs in nature crystallized in figures of the hexagonal system, with the specific gravity, 2.6; these crystals are colorless, or colored by impurities. In the oxy-hydrogen flame it fuses to a transparent glass.

Silicon dioxide is insoluble in water and all acids; but is decomposed by hydrofluoric acid with the formation of silicon fluoride ($SiFl_4$) and water (p. 165). Strong ignition with sodium or potassium reduces it to metallic silicon. The dioxide prepared artificially dissolves when boiled with potassium or sodium hydroxide; some of the naturally occurring amorphous varieties are also soluble, but not the crystallized dioxide. By fusion with the hydroxides or carbonates of the alkalies all varieties of silica yield a glassy mass (water glass) soluble in water and containing silicates (K_4SiO_4 or K_2SiO_3). Upon the addition of hydrochloric acid to the aqueous solution of the potassium or sodium salt, a very voluminous, gelatinous mass separates; this is probably *normal silicic acid*, H_4SiO_4:—

$$Na_4SiO_4 + 4HCl = 4NaCl + H_4SiO_4.$$

It becomes a white amorphous powder having the composition H_2SiO_3 when washed with water and dried in the air. The freshly precipitated acid is somewhat soluble in water, more readily in dilute hydrochloric acid. On adding a solution of sodium silicate to an excess of dilute hydrochloric acid the separated silicic acid remains dissolved. From the hydrochloric acid and sodium chloride solution we can obtain a perfectly pure aqueous solution of silicic acid by dialysis by proceeding in the following manner: Pour the hydrochloric acid solution into a wide cylindrical vessel whose lower opening is covered with animal bladder or parchment paper, and then suspend the vessel (dialyser) in another containing pure water. (Fig. 88.) Osmosis now sets in. The sodium chloride and hydrochloric acid pass through the parchment paper into the outer water, while on the other hand, water passes from the outer vessel into the dialyser; the parchment paper is not permeable to silicic acid. This alternate diffusion of the different particles occurs until the outer and inner liquids show the same quantity of diffusible substances. Upon introducing the dialyser into a fresh portion of water, the dialysis commences anew. Finally, after repeated renewal of the external water, the dialyser will contain a perfectly pure silicic acid solution, free from sodium chloride and hydrochloric acid. The solution may be concentrated by evaporation; it then readily passes into a gelatinous mass. The same occurs instantaneously in dilute solutions if a trace of sodium carbonate be added or carbon dioxide be led into it.

Fig. 88.



Like sodium chloride, all crystallizable soluble substances diffuse through parchment. These are known as *crystalloids*, to distinguish them from the non-diffusible colloids. To the latter belong gum, gelatine, albumen, starch, glue (κόλλα, hence the name colloid), and especially most of the substances which occur chiefly in vegetable and animal organisms. Like silicic acid these colloids exist in liquid, soluble, and solid gelatinous condition. Many other substances (like ferric and aluminium oxides) which ordinarily are insoluble, can be brought into aqueous solution by dialysis.

We have already seen that acids like sulphuric, phosphoric, and arsenic, are capable of forming anhydro- or poly-acids by the union of several molecules and the elimination of water. Silicic acid is particularly inclined to that kind of condensation. It forms a large number of *poly-silicic acids*, $Si_2O_3(OH)_2$, $Si_3O_4(OH)_4$, $Si_3O_5(OH)_2$, etc., derived from the normal and ordinary acid, according to the common formula:—

$$m\mathrm{Si(OH)_4} - n\mathrm{H_2O}.$$

These poly-acids are not known free; it appears, however, that many amorphous forms of silica occurring in nature, as agate, chalcedony, opal, which lose 5–15 per cent. H_2O by ignition, represent such poly-acids. The natural *silicates* are the salts of such acids. The majority are derived from the acids: $H_2Si_2O_5$, $H_4Si_3O_8$, $H_2Si_3O_7$, $H_4Si_4O_9$, and others. Only a few silicates are obtained from the normal acid, *e. g.*, chrysolite—Mg_2SiO_4.

Corresponding to CS_2 is

Silicon Disulphide, SiS_2, which may be made by heating amorphous silicon with sulphur, or by conducting sulphur vapors over an ignited mass of silica and carbon. It sublimes in shining, silky needles, which water changes to silicic acid and hydrogen sulphide.

Germanium, Tin, and **Lead** also belong to the group of carbon and silicon. Their oxygen compounds, MeO_2 and $Me(OH)_4$, are perfectly analogous to those of the latter elements. The metallic character is, however, more pronounced in germanium, tin, and lead, and becomes more noticeable as the atomic weight increases. Germanium and tin form lower oxides, GeO and SnO, which manifest a perfectly basic nature and unite with acids to form salts; therefore germanium, tin, and lead will be discussed under the metals.

TITANIUM.	ZIRCONIUM.	THORIUM.
Ti = 48.1.	Zr = 90.7.	Th = 232.4.

The same relation that vanadium, niobium, and tantalum show to the elements of the phosphorus group, is manifested by the three elements, titanium, zirconium, and thorium, for the silicon group. (See Periodic System, p. 249.)

P = 31.03 V = 51.2 Si = 28.4 Ti = 48.1
As = 75 Nb = 94.2 Ge = 72.3 Zr = 90.7
Sb = 120.3 T = 183 Sn = 118.1 Th = 232.4.

In all their deportment they strongly resemble tin; they possess, however, a more metallic character in their derivatives. They are tetravalent, affording compounds of the form MeX_4, in which X represents monovalent elements and groups; those of the form MeX_2, corresponding to the stannous derivatives, are unknown. The hydroxides, $Me(OH)_4$ and $MeO(OH)_2$, have a stronger basic nature than stannic acid and form stable salts with acids; the basicity increases successively with the atomic weights, in the order, Ti,Zr,Th. Corresponding to this, the acidity of the hydrates, *i. e.*, their capability of exchanging H for metals, gradually diminishes. Thorium hydroxide, $Th(OH)_4$, is not able to form metallic salts.

TITANIUM.

Ti = 48.1

This metal occurs in nature as titanium dioxide (rutile, anatase, brookite) and in titanates (perofskite, TiO_3Ca, menaccanite, $FeTiO_3$). Free titanium is a gray, metallic powder, obtained by heating potassium titan-fluoride (K_2TiFl_6) with potassium. It burns when heated in the air, and decomposes water on boiling. It dissolves in dilute hydrochloric and sulphuric acids, with evolution of hydrogen.

Titanium Chloride—$TiCl_4$—is formed, like silicon chloride, by conducting chlorine over an ignited mixture of the dioxide and carbon. A colorless liquid, of specific gravity 1.76, fuming strongly in the air (with decomposition into hydrochloric and titanic acids), and boiling at 136°. The vapor density equals 95 ($H = 1$), corresponding to the molecular formula $TiCl_4 = 190$. It behaves like tin tetrachloride with water. A compound Ti_2Cl_6, analogous to C_2Cl_6, is known.

Titanium Fluoride—$TiFl_4$—is not known in a free condition, but forms beautifully crystallized double salts, *e.g.*, $TiFl_4, 2KFl$, corresponding to the silicofluorides (K_2SiFl_6).

Titanic Acid—H_4TiO_4—separates as a white, amorphous powder, on adding ammonium hydroxide to the hydrochloric acid solution of the titanates. When dried over sulphuric acid it loses 1 molecule H_2O and becomes $TiO(OH)_2$. Titanic acid, like silicic and stannic acids, forms poly-acids. The hydrates dissolve in alkalies and strong acids, to form salts. On igniting the hydroxides we get

Titanium Dioxide—TiO_2, which may be procured crystallized as rutile, brookite, and anatase. When ignited in a stream of hydrogen it changes to the oxide Ti_2O_3. Titanium dioxide is almost insoluble in the acids; it is only dissolved by hydrofluoric acid. It forms titanates upon fusion with the alkalies.

The hydroxides, TiO_4H_4, TiO_3H_2, etc., conduct themselves as feeble bases with strong acids and afford salts with them (*e. g.*, $TiO.SO_4$), which are decomposed by water. The alkaline titanates (K_2TiO_3) are very unstable. Other titanates occur in nature, *e. g.*, $CaTiO_3$, $MgTiO_3$, and the so-called Titanic Iron, $FeTiO_3$.

Titanium also forms derivatives after the types, Ti_2O_3 and TiO, *e.g.*, Ti_2Cl_6 and $TiCl_2$. The sesquioxide compounds are usually green or violet in color, while those of the monoxide form are black or brown.

Titanium yields various compounds with nitrogen. When the dioxide is heated in ammonia gas, a dark violet powder of the composition TiN_2 results. The compound Ti_5CN_4—the so-called cyan-titanium nitride—is sometimes found in copper-red, metallic cubes, in blast-furnace slag, when iron ores, containing titanium, have been fused.

ZIRCONIUM.

Zr = 90.7.

Zirconium is very rare in nature, but is generally found in silicates, and especially as zircon, $ZrSiO_4$. Zirconium is obtained free in the same way as titanium, and may be isolated as an amorphous black powder or in crystalline metallic leaflets of specific gravity 4.15. Zirconium tetrachloride—$ZrCl_4$, and fluoride, $ZrFl_4$—are very similar to the corresponding titanium compounds.

Zirconic Acid or Hydroxide—$Zr(OH)_4$—is precipitated by ammonium hydroxide, from acid solutions as a white voluminous precipitate, which becomes ZrO_2, zirconium dioxide, upon ignition. Zirconic acid, when fused, is insoluble in potassium and sodium hydroxides; it yields zirconates, Na_2ZrO_3 and Na_4ZrO_4, with the alkalies and their carbonates. Water decomposes these salts.

The oxide and hydroxide dissolve when warmed with sulphuric acid, forming $Zr(SO_4)_2$, which may be crystallized from water.

THORIUM.

Th = 232.4.

Occurs very rarely, mostly in silicates (Thorite). Free thorium, separated by sodium from the double chloride of potassium and thorium ($ThCl_4.2KCl$), is a light-gray, crystalline powder, of specific gravity 11.0, which burns in the air to the dioxide. Its specific heat equals 0.027, corresponding to the atomic weight 232.

Thorium Hydroxide, $Th(OH)_4$, and **Thorium Dioxide**, ThO_2, do not form salts with the alkalies. They dissolve in sulphuric acid to the sulphate, $Th(SO_4)_2$, which crystallizes from water with nine molecules of water. Thorium chloride, $ThCl_4$, is produced by the action of hydrochloric acid gas upon metallic thorium; its formula accords with its vapor density (Nilson).

BORON.

B = 11.01.

This element is generally classed with the metalloids, and stands isolated among them; it forms the transition from these to the metals, which is manifest from its position in the periodic system. On the one side, especially when free, it resembles carbon and silicon; on the other, it approaches the metals, beryllium, aluminium, and scandium (see the Periodic System of the Elements). As recently observed, it affords a gaseous hydride, but it is not very stable, and, like stibine, may be easily decomposed into its constituents. Its oxide, B_2O_3, although really of an acid nature, approaches such metallic oxides as aluminium oxide, Al_2O_3, which functionates both as base and acid. Boron is trivalent, and yields only compounds of the form BX_3.

It is found in nature as boracic acid and in the form of borates, like borax (sodium salt), boracite (magnesium salt). It may be obtained free in an amorphous and crystallized state. The first results upon igniting boron trioxide with sodium away from air contact; free boron and sodium borate are produced. On treating the fusion with water the borate dissolves, leaving the metal as a greenish-brown powder, which, when heated in the air, burns with strong brilliancy to the trioxide. Nitric and sulphuric acids change it to boric acid. When fused with phosphoric acid it liberates phosphorus. Upon boiling with aqueous alkalies it dissolves, like beryllium, silicon and aluminium, with formation of borates:—

$$2B + 2KOH + 2H_2O = 2BO.OK + 3H_2.$$

Amorphous boron can also be obtained quite readily by mixing 100 grams of fused and finely divided borax with 50 grams of magnesium powder, the mixture being filled into a Hessian crucible, pressed down, and covered with a layer of pure borax. The crucible is well covered and exposed to a red heat for fifteen minutes. After cooling the product is pulverized and boiled with water, then with hydrochloric acid, and again with water. The dry mass is gray-brown in color (*Berichte*, 22, 195).

The *crystalline* variety may be obtained by igniting boron trioxide with aluminium. The boron, separated by the aluminium, dissolves in excess of the latter, and crystallizes from it on cooling; upon dissolving the aluminium in hydrochloric acid the boron remains in shining, transparent, quadratic crystals, which are more or less colored, and have a specific gravity of 2.63. The crystals are not pure boron, but contain aluminium and carbon. In their lustre, refraction of light, and hardness, they resemble the diamond. Crystalline boron is more stable than the amorphous; it does not oxidize upon ignition, and is only slightly attacked by acids. Fused with potassium and sodium hydroxide both modifications yield borates.

Boron Hydride, BH_3. It has recently been ascertained that boron, like the other metalloids, can yield a gaseous product with hydrogen. It results when hydrochloric acid acts upon magnesium boride. The latter is obtained by heating boron, boric anhydride, or boron chloride, with magnesium dust. A colorless gas is evolved which, besides much hydrogen, contains some boron hydride, and burns with a bright green flame, with separation of boric anhydride. When the gas is conducted through a red-hot tube, or on holding a cold porcelain plate in the flame, boron deposits as a brown sublimate. It produces a black precipitate, containing silver and boron, when it is conducted into a solution of silver nitrate.

Boron Trichloride, BCl_3, may be prepared by heating boron in chlorine, or conducting a stream of the latter over an ignited mixture of the trioxide and carbon (see $SiCl_4$ and Al_2Cl_6):—

$$B_2O_3 + 3C + 3Cl_2 = 2BCl_3 + 3CO.$$

It is a colorless liquid, of specific gravity 1.35, and boiling at 18°. Its vapor density equals 58 ($H = 1$), corresponding to the molecular formula $BCl_3 = 117$. The liquid fumes strongly in the air and decomposes with water into boric and hydrochloric acids:—

$$BCl_3 + 3H_2O = B(OH)_3 + 3HCl.$$

The trichloride also results from the action of the pentachloride of phosphorus upon the trioxide:—

$$B_2O_3 + 3PCl_5 = 2BCl_3 + 3POCl_3.$$

Boron Fluoride, BFl_3, is similar to silicon fluoride, and is produced according to the same methods, by the action of hydrofluoric acid upon the trioxide, by warming a mixture of the trioxide and calcium fluoride with sulphuric acid—

$$B_2O_3 + 3CaFl_2 + 3H_2SO_4 = 3CaSO_4 + 3H_2O + 2BFl_3,$$

or by exposing amorphous boron to a gentle heat while conducting dry chlorine gas over it (*Berichte*, 22, 195).

It is a colorless gas, fuming strongly in the air, of specific gravity 34 ($H = 1$), and may be condensed to a liquid under strong pressure. It dissolves very readily in water (700 volumes in 1 vol.), producing **Hydrogen Boro-fluoride**, BFl_4H ($= BFl_3.FlH$), which remains in solution:—

$$4BFl_3 + 3H_2O = 3HBFl_4 + H_3BO_3.$$

The reaction is analogous to the formation of hydrofluo-silicic acid from silicon fluoride (see p. 165). Hydrogen borofluoride is a monobasic acid, only known in solution and in its salts.

Boric Acid—$H_3BO_3 = B(OH)_3$—occurs free in nature and in salts. In some volcanic districts, especially in Tuscany, steam escapes from the earth (fumeroles, etc.) containing small quantities of it. These vapors condense in small natural water pools, or are conducted into walled basins. By evaporation, and concentration of the aqueous solution, boric acid separates; the same occurs naturally as sassolite. To prepare pure boric acid, precipitate a hot solution of borax with hydrochloric acid. The acid separates in colorless, shining scales; it dissolves in 25 parts H_2O at 14°, or in 3 parts at 100°. The solution shows a feeble, acid reaction with litmus; turmeric paper, moistened with it, is colored red-brown after drying. On boiling the solution, boric acid escapes with the steam. An alcoholic solution of the acid burns with a green flame. These reactions afford a ready means for its detection.

When heated to 100°, the acid loses 1 molecule of H_2O, and passes into the anhydro- or meta-acid, HBO_2, which at 140° is converted into Tetraboric acid—$B_4O_7H_2$. When ignited, boric anhydride or *Boron trioxide*, B_2O_3, is produced. This is a fusible, glassy mass, of specific gravity 1.8, and is slightly volatile at a very high heat. Water dissolves the anhydride to boric acid.

It is a very weak acid; and can be expelled from its salts by most other acids. By fusion it removes the most acids from their salts, in consequence of the difficult volatility of its anhydride.

Salts of normal boric acid, $B(OH)_3$, are not known, while the ethers, $B(O.CH_3)_3$, are. The salts of metaboric acid, $BO.OK$, can be obtained crystallized, but they are very unstable. They are decomposed by carbon dioxide with production of salts of tetraboric acid:—

$$4NaBO_2 + CO_2 = B_4O_7Na_2 + CO_3Na_2.$$

The latter, from which the ordinary borates are derived (see Borax), may be viewed as an anhydro-acid, produced by the union of 4 molecules of trihydric boric acid (compare p. 197):—

$$4B(OH)_3 - 5H_2O = B_4O_7H_2.$$

On heating amorphous boron in a stream of N or ammonia, or by igniting a mixture of the trioxide and carbon in nitrogen gas, there is formed *boron nitride*, BN. This is a white amorphous powder, which gives forth an extremely intense greenish-white light when heated in a flame. Boric acid and ammonia result when steam at 200° is conducted over the nitride :—

$$BN + 3H_2O = B(OH)_3 + NH_3.$$

PERIODIC SYSTEM OF THE ELEMENTS.

In the preceding pages we have studied four groups of elements and their compounds with hydrogen, the halogens and oxygen. We have repeatedly directed attention to the remarkable relations of the elements of a single group, as well as to those of the various groups to each other, but they appear more manifest if viewed in the connection in which they present themselves in the *periodic system of elements*. The position which these elements occupy in this system determines their entire physical and chemical character to a marked degree.

The system is based upon the grouping of the elements according to the magnitude of their atomic weights. For the longest time we have been cognizant of the remarkable relations existing between the atomic weights of analogous elements, but only recently has the *law of periodicity* underlying them been announced by Mendelejeff and Lothar Meyer, and, according to this, *the properties of the elements* and their compounds present themselves *as periodic functions of the atomic weights.*[*]

Arranging the elements according to increasing atomic weight we observe that similar elements return after definite intervals. Thus they arrange themselves in several periods, consisting of the following horizontal series (for brevity the atomic weights are not attached to the symbols) :—

1.	Li	Be	B	C	N	O	Fl
2.	Na	Mg	Al	Si	P	S	Cl

3.	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
4.	Rb	Sr	Y	Zr	Nb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
5.	Cs	Ba	(La	Ce	Di)	—	—	—	—	—	—	—	—	—	—	—	—
6.	—	—	Yb	—	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	—	—
7.	—	—	—	Th	—	Ur	—	—	—	—	—	—	—	—	—	—	—

The first two series, lithium (Li) to fluorine (Fl), and sodium (Na) to chlorine (Cl), present two periods of seven members each,

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[*] John A. B. Newlands published similar views as early as 1865. He recognized that every seventh element was an analogue of the first, and called these relations the law of octaves (see On the Discovery of the Periodic Law, by John A. B. Newlands, 1884).

in which the corresponding (above and below) members exhibit a great but not complete analogy. Sodium resembles lithium; magnesium, beryllium; chlorine, fluorine, etc. Then follow two periods, consisting of 17 elements each: potassium (K) to bromine (Br), and rubidium (Rb) to iodine (I). The series 5 and 6 are incomplete, and together probably constitute a period. In the 7th series there are as yet but two elements: thorium = 232 and uranium = 240. Thus result 3 *great periods*, whose corresponding members exhibit an almost complete analogy: the elements K Rb Cs, Ca Sr Ba, Ga In Tl, As Sb Bi, etc., are so similar that they remind us of the homologous series of the carbon compounds (compare p. 155), and, therefore, can be designated as *homologous* elements. It is only in the third great period (series 5 and 6) that the middle members exhibit any variations.

Now on comparing the three great periods with the two small ones, we discover that the first members are analogous to each other: K,Rb,Cs resemble Na and Li; Ca,Sr,Ba resemble Mg and Be. Then the similarity gradually lessens, disappears apparently in the middle members, and only appears again toward the end of the periods: I and Br resemble chlorine and fluorine; Te and Se, sulphur and oxygen; Bi, Sb, As, phosphorus and nitrogen, etc. The character or the function of the three great periods is therefore other than that of the two small periods. But in all five periods we can detect a gradual, regular alteration in the properties of the adjoining *heterologous* elements. This is particularly manifest in the measurable physical properties, all of which show a maximum or minimum in the middle of the periods (both of the great and small), as may be seen, for example, in the specific gravity of the elements in solid condition (compare further the atomic volumes, p. 258):—

	Na	Mg	Al	Si	P	S	Cl
Specific gravity,	0.67	1.7	2.5	2.5	2.0	1.9	1.3

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
0.86	1.6	3.8	—	5.5	6.8	7.2	7.9	8.5	8.8	8.8	7.1	5.9	5.5	5.6	4.6	2.9.

These relations show themselves very clearly in a graphic representation, by making the atomic weights the abscissas, the numerical values of the properties the ordinates; then the individual periods represent segments of curves, which blend to a curve with alternating maxima and minima.

The same regularity exhibits itself even in chemical properties, in the two small periods, especially in the valence of the elements in their compounds with hydrogen or the hydrocarbon groups CH_3,C_2H_5, etc. (compare p. 176 and p. 251). The hydrogen valence rises and falls periodically with the condensation of the substance (corresponding to the specific gravity):—

$$\overset{\text{I}}{\text{NaR}}\quad \overset{\text{II}}{\text{MgR}_2}\quad \overset{\text{III}}{\text{AlR}_3}\quad \overset{\text{IV}}{\text{SiH}_4}\quad \overset{\text{III}}{\text{PH}_3}\quad \overset{\text{II}}{\text{SH}_2}\quad \overset{\text{I}}{\text{ClH}}.$$

On the other hand, the maximum valence of the elements increases successively in the salt-forming oxides (p. 174):—

$$\overset{\text{I}}{\text{Na}_2\text{O}}\quad \overset{\text{II}}{\text{MgO}}\quad \overset{\text{III}}{\text{Al}_2\text{O}_3}\quad \overset{\text{IV}}{\text{SiO}_2}\quad \overset{\text{V}}{\text{P}_2\text{O}_5}\quad \overset{\text{VI}}{\text{SO}_3}\quad \overset{\text{VII}}{\text{Cl}_2\text{O}_7}.$$

The chemical valence expresses itself somewhat differently in the three great periods. In them we have a *double periodicity;* thus, *e. g.*, with the salt-forming oxides:—

$$\overset{\text{I}}{\text{K}_2\text{O}}\quad \overset{\text{II}}{\text{CaO}}\quad \overset{\text{III}}{\text{Sc}_2\text{O}_3}\quad \overset{\text{IV}}{\text{TiO}_2}\quad \overset{\text{V}}{\text{V}_2\text{O}_5}\quad \overset{\text{VI}}{\text{CrO}_3}\quad \overset{\text{VII}}{\text{Mn}_2\text{O}_7}$$

$$\overset{\text{VI}}{\text{FeO}_3}\quad \overset{\text{IV}}{\text{CoO}_2}\quad \overset{\text{II}}{\text{NiO}}$$

$$\overset{\text{I}}{\text{Cu}_2\text{O}}\quad \overset{\text{II}}{\text{ZnO}}\quad \overset{\text{III}}{\text{Ga}_2\text{O}_3}\ \overset{\text{IV}}{—}\ \overset{\text{V}}{\text{As}_2\text{O}_5}\quad \overset{\text{VI}}{\text{SeO}_3}\quad \overset{\text{VII}}{\text{Br}_2\text{O}_7}.$$

In consequence of this double periodicity, the first seven and the last seven members of the three great periods, with respect to their valence (and consequently also their compounds), resemble the seven members of the two small periods. To bring out this double periodicity and analogy, the first seven and last seven members of the great periods are divided into two series, and arranged under the corresponding seven members of the small periods.

In this way the three middle members of the great periods (which are found between the dotted lines of the table, p. 246) come to stand apart, as they have no analogues. In this manner arises the following table, in which the seven (or ten) vertical columns include analogous elements:—

Li		Be		B		C		N		O		Fl				
Na		Mg		Al		Si		P		S		Cl				
K		Ca		Sc		Ti		V		Cr		Mn		Fe	Co	Ni
	Cu		Zn		Ga		Ge		As		Se		Br			
Rb		Sr		Y		Zr		Nb		Mo		—		Ru	Rh	Pd
	Ag		Cd		In		Sn		Sb		Te		I			
Cs		Ba		La		(CeDi)		—				—				
	—		—	Yb			—	Ta		W		—		Os	Ir	Pt
	Au		Hg		Tl		Pb		Bi		—		—			

The Periodic System of the Elements.

		I Group.	II Group.	III Group.	IV Group.	V Group.	VI Group.	VII Group.	VIII Group.		
H-Compounds. Highest salt-forming oxides.		— M_2O	— MO	— M_2O_3	MH_4 MO_2	MH_3 M_2O_5	MH_2 MO_3	MH M_2O_7	MO_3	MO_2	(M_2H) MO
Periods.	Series.										
1st	1st	H 1 Li 7	Be 9	B 11	C 12	N 14	O 16	Fl 19			
2d	2d	Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35.4			
3d	3d	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56	Co 58	Ni 58
	4th	Cu 63	Zn 65	Ga 70	Ge 72	As 75	Se 79	Br 79.7			
4th	5th	Rb 85	Sr 87	Y 89	Zr 90	Nb 94	Mo 96	— 100	Ru 104	Rh 104	Pd 106
	6th	Ag 108	Cd 112	In 113	Sn 117	Sb 120	Te 126	I 126.5			
5th	7th	Cs 133	Ba 137	La 139	(Ce 140	Di 142)	—	(Sa 150)?	—	—	—
	8th	—	—	—	(Er 166) ?	—	—	—			
	9th	—	—	Yb 173	—	Ta 182	W 184	—	Os(195)	Ir 193	Pt 195
	10th	Au 197	Hg 200	Tl 204	Pb 206	Bi 210	—	—			
		—	—	—	Th 232	—	Ur 240	—			

In the preceding table (p. 249) we have presented the same grouping of the elements, together with their atomic weights, given in round numbers. In this arrangement we must always bring into consideration that the principal analogy (homology) of the three great periods finds expression in the three uninterrupted horizontal series (p. 246), and that the decomposition of the latter into two series each only corresponds to the secondary, double analogy with the small periods. It may be further remarked that, in the second small period the last three members, P, S and Cl, show a complete homology with the corresponding members of the large periods—as is represented in the table.

When the periodic grouping of the elements was first presented, some atomic weights, not sufficiently well established at that time, had to be more or less altered. Thus, the atomic weight of indium, formerly 75.6, was made 113.4, and that of uranium 240 (before 120). All such alterations have been proved to be established through recent investigations. Further, the atomic weight of tellurium (formerly determined to be 128) had to be less than that of iodine (126.5); this, also, has been established by recent researches, which place it at 125 (p. 114). There is, therefore, little doubt that the atomic weight of osmium (found 195) will also prove to be somewhat less. This is only the more likely, since it has been shown that the atomic weight of iridium, which was formerly given as 197, is really 192.7. Hence, the periodic system offers a control for the numbers of the atomic weight, while formerly they appeared to be irregular, and, at the same time, accidental.

Further, upon the basis of the periodic system, the existence of new, not yet known, elements may be ascertained, which correspond to unoccupied, free places or gaps in the table. In fact, three such gaps have been filled up by the discovery of gallium (Ga = 69.8), scandium (Sc = 44), and germanium (Ge = 72.3); their properties have shown themselves to be perfectly accordant with those deduced from the periodic system. At present, only the first homologue of manganese (with atomic weight of about 100) is wanting. The series 5 and 6 are very incomplete: the elements, terbium, samarium, and erbium, little investigated as yet, will probably find positions in them. It may be, however, that the two series will together form a single period of somewhat varying character. Consult further *Annalen der Chemie*, 8 Supplement Band, p. 133.

The entire character of a given element is determined to a very high degree by the law of periodicity; hence, all physical and chemical properties of the same are influenced by its position in the system. These relations we will examine more closely in the individual groups of the elements, and here confine ourselves to a notice of some general relations, and the connection of atomic weight with the chemical valence of the elements and the thermo-chemical phenomena.

The relation of metalloids to metals is shown with great clearness in the periodic system. The first members of all periods (on the left side) consist of electro-positive metals, forming the strongest bases, the alkalies—Cs, Rb, K, Na, Li, and metals of the alkaline earths—Ba, Sr, Ca, Mg, and Be. The basic character diminishes successively, in the following heterologous members, and gradually passes over into the electro-negative, acid-forming character of the metalloids, Fl, Cl, Br, I. Here is observed that, in the periods following each other, with higher atomic weights, the basic metallic character constantly exceeds the metalloidal. The first period comprises five metalloids (B, C, N, O, Fl), the second only four (Si, P, S, Cl), the fourth and fifth periods each only three (or two) metalloids (As, Se, Br, and Sb, Te, I), which, at the same time, become less negative. With the metalloidal nature is combined the power of forming volatile hydrogen compounds. Similar volatile derivatives are also afforded by the metalloids with the monovalent hydrocarbon groups (as CH_3, C_2H_5, C_3H_7, etc.), which resemble hydrogen in many respects. Such metallo-organic compounds, in which the elements show the same valence as in the hydrogen compounds, are also produced by the metals adjacent to the metalloids:—

$$\overset{II}{Mg}(CH_3)_2,\ \overset{III}{Al}(CH_3)_3,\ \overset{IV}{Si}(CH_3)_4,\ \overset{III}{P}(CH_3)_3,\ \overset{II}{S}(CH_3)_2,\ \overset{I}{Cl}CH_3.$$

Their stability gradually diminishes with the increasing basic nature of the metals; hence, in the three large periods, this power extends only to Zn, Cd, and Hg.

In consequence of the opposite (metalloidal and metallic) character of the two ends of the periods, there are in the table representing the double periodicity of the great periods (pp. 248 and 249) two sub-groups each, with the seven vertical groups; on the left with the more positive, basic, and on the right with the more negative, metalloidal elements. Thus in group VI, in addition to O and S (belonging to the small periods) stands the more basic sub-group Cr, Mo, W, and the metalloids Se and Te; in group II stand the strong basic metals Ca, Sr, Ba, and the less basic heavy metals, Zn, Cd, Hg. The elements of group VIII form the gradual transition from the latter to the former.

* * *

The fundamental deduction necessarily resulting from the law of periodicity is, that the various elementary atoms must be aggregations or condensations of one and the same primordial substance, a necessary correlative postulate of the recognized unity of all forces. Then only can we comprehend that the properties of the elements are functions of the atomic weight. It was once believed that this primordial substance was hydrogen (hypothesis of Prout), because it seemed that the numbers representing the atomic weights were all whole numbers (multiples of the hydrogen atom = 1). The most accurate determinations, made with exceeding care by Stas, prove that this is not correct in all instances. It is, however, noteworthy that of the 18–20 elements whose atomic weights have been carefully established, ten (Li, K, Na, C, O, S, N, etc., — p. 24), so nearly approach whole numbers, that a complete coincidence is not unlikely. It is possible that these elements represent multiples of the hydrogen atom. We can only expect to arrive at the underlying law when the atomic numbers of a majority of the elements have been determined with equal accuracy.

Periodicity of Chemical Valence.—Group I of the table comprises the monovalent metals, group II the divalent. In group III are the trivalent metalloid, boron, and the trivalent metals Al, Sc, Y, and Ga, In, Tl. In the tetravalent carbon group the valence arrives at its maximum; from here it gradually decreases with increasing atomic weight; the nitrogen group is trivalent, the oxygen group is divalent, that of the halogens monovalent. This valence is derived from the compounds with hydrogen and hydrocarbons (compare p. 251), or where such do not exist, as in the case of boron and many metals, from the halogen compounds:—

			$\overset{\mathrm{IV}}{\mathrm{CH_4}}$	$\overset{\mathrm{III}}{\mathrm{NH_3}}$	$\overset{\mathrm{II}}{\mathrm{OH_2}}$	$\overset{\mathrm{I}}{\mathrm{FlH}}$
$\overset{\mathrm{I}}{\mathrm{LiCl}}$	$\overset{\mathrm{II}}{\mathrm{BeCl_2}}$	$\overset{\mathrm{III}}{\mathrm{BCl_3}}$	$\overset{\mathrm{IV}}{\mathrm{CCl_4}}$	$\overset{\mathrm{III}}{\mathrm{NCl_3}}$	$\overset{\mathrm{II}}{\mathrm{OCl_2}}$	$\overset{\mathrm{I}}{\mathrm{Fl_2}}$
NaCl	$\mathrm{MgCl_2}$	$\mathrm{AlCl_3}$	$\mathrm{SiCl_4}$	$\mathrm{PCl_3}$	$\mathrm{SCl_2}$	$\mathrm{Cl_2}$.

The elements of the first four groups are not capable of yielding higher compounds with the halogens. On the other hand, as we have seen, the higher analogues of nitrogen and other metalloids can unite with a larger number of halogen atoms (see p. 171). The higher valence of these elements is more manifest in the more stable oxygen compounds. On bringing together the *highest oxides* of the seven groups capable of forming salts (salt-building oxides), we get this series:—

$$\overset{\mathrm{I}}{\mathrm{Li_2O}} \quad \overset{\mathrm{II}}{\mathrm{BeO}} \quad \overset{\mathrm{III}}{\mathrm{B_2O_3}} \quad \overset{\mathrm{IV}}{\mathrm{CO_2}} \quad \overset{\mathrm{V}}{\mathrm{N_2O_5}} \quad \overset{\mathrm{VI}}{\mathrm{SO_3}} \quad \overset{\mathrm{VII}}{\mathrm{I_2O_7}}.$$

The elements of the first four groups in their oxygen compounds exhibit, consequently, the same valence as in the compounds with hydrogen (or hydrocarbon radicals) and the halogens; in the last three series, however, there is noticed a constant increase of valence for oxygen.

Besides these highest oxides, remarkable for their greater stability, the elements of the last three groups afford lower oxides, returning in this manner to the hydrogen valence :—

$$\begin{array}{ccc} \overset{III}{P}_2O_3 & \overset{IV}{S}O_2 & \overset{V}{I}_2O_5. \\ & \overset{II}{S}Cl_2 & \overset{III}{Cl}_2O_3. \\ & & \overset{I}{Cl}_2O. \\ \hline \\ PH_3 & SH_2 & ClH. \end{array}$$

The hydroxyl compounds of the elements of the 7 groups are analogous to the oxides in constitution. They afford the following series, expressing the maximum valence (compare p. 174) :—

$$\overset{I}{Na}(OH) \quad \overset{II}{Mg}(OH)_2 \quad \overset{III}{Al}(OH)_3 \quad \overset{IV}{Si}(OH)_4 \quad \overset{V}{P}(OH)_5 \quad \overset{IV}{S}(OH)_6 \quad \overset{VII}{Cl}(OH)_7.$$

The hydroxyl compounds of the elements of the first 4 groups exist in free condition, excepting that of carbon, $C(OH)_4$, which is only represented in its derivatives. The strong basic character of the hydroxides of group I (NaOH) diminishes, step by step, in the succeeding groups, down to the weak acid hydrate, $Si(OH)_4$. The hydrates of the last three groups are of acid nature, and mostly unstable or not known. By elimination of 1, 2 and 3 molecules of H_2O, they yield the ordinary highest acids :—

$$\begin{array}{ccc} \overset{V}{P}O(OH)_3 & \overset{VI}{S}O_2(OH)_2 & \overset{VII}{Cl}O_3OH. \\ \text{Phosphoric acid.} & \text{Sulphuric acid.} & \text{Perchloric acid.} \end{array}$$

The non-saturated hydroxides behave in the same way :—

$$\begin{array}{ccc} \overset{III}{P}(OH)_3 & \overset{IV}{S}(OH)_4 & \overset{V}{Cl}(OH)_5 \\ & \overset{II}{S}(OH)_2 & \overset{III}{Cl}(OH)_3 \\ & & \overset{I}{Cl}(OH). \end{array}$$

Sulphurous acid, $SO(OH)_2$ (p. 189), is derived from the hydrate, $S(OH)_4$; chloric acid, $ClO_2.OH$, from the hydrate, $Cl(OH)_5$; and chlorous acid, $ClO.OH$, from the hydrate, $Cl(OH)_3$ The hydrates, $P(OH)_3$, $S(OH)_2$ and $ClOH$, are very unstable, and the first two appear to pass readily into $HPO(OH)_2$ and $HSO.OH$ (compare p. 187).

It has been shown already in the case of periodic, sulphuric, and nitric acids, how the so-called hydrates with water of crystallization (regarded as molecular compounds) are explained by the acceptance of the existence of such hydroxyl derivatives. The same may be done for many salts with water of crystallization.

Thus, we see, and in the following pages will find it more extensively developed, that the relations of valence of the elements have their complete expression in the periodic system, are regulated by it, and hence we must conclude that, in fact, the valence is not only a property attaching to the elements *per se*, but is influenced also by the nature of the combining elements: the hydrogen valence is constant, the valence to oxygen and the halogens, on the contrary, varies according to definite rules. Valence, therefore, is a relative function of the elements (p. 174).

Periodicity of Thermo-Chemical Phenomena. We observed in the case of the elements of the chlorine and sulphur group, that, in their hydrogen compounds the heat liberation decreased successively with increasing atomic weight (pp. 66 and 116), while there is generally an increase in their oxygen derivatives (pp. 178 and 186). Similar relations exhibit themselves with the halogen, oxygen, and sulphur compounds of the metals, as will be more fully exemplified later with the individual groups. Here it is sufficient to call attention to the relations in the heterologous series.

In the formation of the hydrogen compounds of the elements of the first two periods, the following quantities of heat are set free according to present data :—

(C,H_4)	(N,H_3)	(O,H_2)	(Fl,H)
21.7	11.9	57.2	—
(Si,H_4)	(P,H_3)	(S,H_2)	(Cl,H)
33.2	11.6	4.5	22.0

In the halogen compounds the heat modulus is more regular :—

(Li,Cl)	(Be,Cl_2)	(B,Cl_3)	(C,Cl_4)	(N,Cl_3)	(O,Cl_2)	(Fl,Cl)
93.8	—	104	28.3	—38.1	—18	—
(Na,Cl)	(Mg,Cl_2)	(Al,Cl_3)	(Si,Cl_4)	(P,Cl_3)	(S,Cl_2)	(Cl,Cl)
97.7	151.0	160.9	157.6	75.3	—	—

With the bromides, it is less throughout, and the least with the iodides. Consequently, a maximum appears to lie in the middle of the periods. However, on calculating the thermal value, which corresponds to one equivalent of the elements (united with one equivalent of chlorine), we obtain numbers that diminish successively and correspond to the decrease of the basic metallic character of the elements :—

(Na,Cl)	$\left(\frac{Mg,Cl_2}{2}\right)$	$\left(\frac{Al,Cl_3}{3}\right)$	$\left(\frac{Si,Cl_4}{4}\right)$	$\left(\frac{P,Cl_3}{3}\right)$	$\left(\frac{S,Cl_2}{2}\right)$	$(Cl,Cl).$
97.7	75.5	53.6	39.4	25.1	——	——

Perfectly similar relations are furnished by the oxides :—

(Na_2,O)	(Mg,O)	(Al_2,O_3)	(Si,O_2)	(P_2,O_5)	(S,O_3)	$(Cl_2,O_7).$
(100.2)	145.8	388.8	219	363	104	——

Calculated upon one equivalent, the thermal value is :—

50.1	72.9	64.6	54.7	36.3	17.3	—

That the heat disengaged in sodium oxide is less than that in magnesium oxide, depends partly upon the solubility of the first, as this property is also to be included as a thermal function. A like diminution of the heat modulus is also seen with the heterologous elements in their compounds of similar type :—

(Mn, Cl_2)	(Fe, Cl_2)	(Co, Cl_2)	(Ni, Cl_2)	(Cu, Cl_2)	(Zn, Cl_2)
111.9	82	76.4	74.5	51.6	97.2
(Mn, O)	(Fe, O)	(Co, O)	(Ni, O)	(Cu, O)	(Zn, O)
94.7	68.2	63.4	60.8	37.1	85.4

The following series are also noteworthy :—

(Ag, Cl)	(Cd, Cl_2)	(In, Cl_3)	(Sn, Cl_4)	(Sb, Cl_3)	(Te, Cl_2)
29.3	93.2	——	127.2	87	——
(Ag_2, O)	(Cd, O)	(In_2, O_3)	(Sn, O_2)	(Sb_2, O_3)	(Te, O)
5.9	65.6	——	133.5	——	——

THE REDUCTION OF METALLIC OXIDES BY METALLIC MAGNESIUM.

Winkler has made interesting observations upon the deportment of metallic magnesium toward the oxides, hydroxides, and carbonates of the metals when heated together and in the presence of hydrogen. His results are briefly as follows:—

Magnesium heated in contact with the oxides, hydroxides, and carbonates of the alkali metals causes their reduction to the metallic condition; cæsium alone is excepted. The reducing action loses in intensity as the atomic weights of the metals rise. With the oxides of copper, silver, and gold the intensity of reduction increases as the atomic weight rises.

The oxides and hydroxides of beryllium, magnesium, calcium, strontium, and barium are also reduced, but the metals are not volatilized. When the reduction occurs in an atmosphere of hydrogen, *hydrides* of these metals result. The production of the hydrides of beryllium and magnesium is not very complete. Calcium hydride is more readily produced and in considerable quantity, while the union of hydrogen with strontium and barium is more easily effected and the yield of product much greater. These hydrides are all earthy masses, without lustre.

The oxides of zinc, cadmium, and mercury are reduced with much energy. The heat of reduction causes either a partial or entire volatilization of the corresponding metals.

Magnesium heated together with boron trioxide and borax yields a magnesium boride of varying composition. Aluminium oxide is converted into a product that contains a monoxide of aluminium. Yttrium and lanthanum are both apparently reduced; they also combine with hydrogen to form hydrides.

The reduction of the oxides of gallium, indium, and thallium by magnesium is very violent; it increases with increasing atomic weight.

Magnesium has a decided preference for carbon, as is evident from its deportment toward carbon dioxide, carbon monoxide, and the carbonates. With silicon, magnesium at low temperatures forms magnesium silicide, while at an intense heat the products are amorphous silicon and magnesium oxide.

Zirconium dioxide, heated together with magnesium in an atmosphere of hydrogen, yields a product black in color, and it may be that a zirconium hydride does exist. Titanium dioxide is reduced to monoxide with the simultaneous production of magnesium titanate. The *hydride* is apparently not formed. Cerium dioxide is reduced to metallic cerium or to the sesquioxide. If the reaction occurs in hydrogen *cerium hydride* is formed. Thorium dioxide is reduced to metal, and in the presence of hydrogen its hydride results.

It would thus appear that *all* the members of the principal division of the quadrivalent elements are capable of yielding hydrides, although it is not so evident with titanium.

More recently Seubert and Schmidt have shown that metallic magnesium is capable of removing the chlorine from metallic chlorides in neutral aqueous solution; the exceptions, in this case, being the chlorides of the alkali and alkaline earth metals. At elevated temperatures, however, all chlorides are reduced by magnesium.

THE METALS.

Although there is no sharp line of demarcation between metals and non-metals, yet these two classes of bodies form a distinct contradiction in their entire deportment, as may be plainly seen in the periodic system of elements. In physical respects the character of metals is determined by their external appearance and by their ability to conduct heat and electricity; chemically, it shows itself chiefly in the basicity of the oxygen compounds; yet we see that with the increase of the number of the oxygen atoms, the basic character gradually diminishes and becomes acidic.

PHYSICAL PROPERTIES OF THE METALS.

At ordinary temperatures all the metals excepting mercury are solid, slightly volatile bodies. They are opaque, and only a few, like gold, permit the passage of light to a limited extent when beaten into thin leaflets. In compact mass they exhibit metallic lustre and mostly possess a whitish-gray color; gold and copper are, however, brilliantly colored. In powder form almost all the metals are black. Most of them crystallize in the forms of the regular system; only a few, showing a metalloidal character, are not regular. Thus antimony and bismuth crystallize in the hexagonal system, and tin is quadratic. The specific gravities of the metals vary greatly—from 0.59 to 22.4 as seen from the following arrangement:—

Lithium,	0.59	Arsenic,	5·67	Silver,	10.5
Potassium,	0.86	Antimony,	6.7	Lead,	11.4
Sodium,	0.97	Zinc,	7.1	Palladium,	11.5
Rubidium,	1.52	Tin,	7·3	Thallium,	11.8
Calcium,	1.58	Iron,	7.8	Mercury,	13·59
Magnesium,	1.75	Cobalt,	8.5	Gold,	19·3
Aluminium,	2.56	Cadmium,	8.6	Platinum,	21.5
Barium,	3·75	Copper,	8.8	Iridium,	22.4
Germanium,	5·47	Bismuth,	9.8	Osmium,	22.4

In general the specific gravities of the metals, and also those of the metalloids, increase with the atomic weights; they stand more especially in sharp periodic dependence with reference to the latter.

The first members of all periods possess low specific gravities; the latter grow gradually until the middle of the period, when the maximum is attained, and then they again decrease (p. 247). These relations show themselves more fully if, instead of the specific gravity, we compare the specific volumes or atomic volumes; *i. e.*, the quotients from the atomic weights (A) and specific gravities (d):—

$$\frac{A}{d} = \text{specific volume.}$$

These quotients express the relative volumes of the atoms (in solid or liquid state). Thus the atomic volume of lithium $\left(\frac{7}{0.59}\right)$ = 11.9, that of potassium $\left(\frac{39}{0.86}\right)$ = 45.4; *i. e.*, the potassium atom occupies a space 3.8 times larger than that of the lithium atom. The periodic alterations of the atomic volumes are set opposite to those of the specific gravities, as the former are obtained by the division of the atomic weights by the specific gravities. Therefore, the atomic volumes decrease gradually, commencing with the first members of the periods (Li, Na, K, Rb), attain a minimum in the middle of the periods, and then increase again up to the last members (Cl, Br, I). On the other hand, we find that with the homologous elements (the vertical series) an increase in the atomic volumes almost invariably occurs as the atomic weights increase.

Since in the three large periods the alterations of the atomic volumes (as well as of all other physical properties) indicate a simple periodicity (not double like the valence), they are expressed in the following tables by progressive series (page 247):—

ATOMIC VOLUMES OF THE ELEMENTS.

Li	Be	B	C*	N	O†	Fl
11.9	5.7	4.1	3.6	—	17	—

Na	Mg	Al	Si	P	S	Cl†
23.7	13.8	10.7	11.2	13.5	15.7	25.6

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
45.4	25.4	12	—	9.3	7.7	6.9	7.2	7.0	6.7	7.2	9.1	11.6	13.3	13.2	17.2	26.9

Rb	Sr	Y	Zr	Nb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
56.1	34.9	—	21.7	15.0	11.1	—	8.4	8.6	9.2	10.2	12.9	15.3	16.1	18.2	20.3	25.6

Cs	Ba	La	Ce	Di	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	36.5	22	21	21																		

—	—	Yb	—	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	—	—
		—	—	16.9	9 6	—	8.3	8.7	9.1	10.2	14.7	17.1	18.1	21.1		

Th	—	Ur
21		13

---

* As diamond.

† Liquid.

It is exceedingly noteworthy, that the elements standing at the beginning and end of the periods (on one side the alkalies, Li, Na, K, Rb, and the alkaline earth metals, Be, Mg, Ca, Sr, Ba, on the other, the halogens and the elements of the oxygen group), possess the greatest chemical energy, and there is scarcely a doubt that an intimate relation exists between chemical energy and atomic volume. We can suppose that the specifically light elements, with large atomic volumes, execute larger chemical oscillations, hence act together more readily and energetically. The fact that greater quantities of heat are eliminated in energetic reactions would harmonize with this idea. It would follow, too, that the expressions of chemical valence between the elements of greater but opposite oscillations (the alkalies and halogens) are the simplest—they behave toward each other as monads.

The metals whose specific gravity is less than 5 are termed *light*, the rest *heavy*. The former usually possess a greater chemical energy, therefore oxidize more easily and form strong basic oxides; their compounds dissolve readily. On the whole, the heavy metals possess a varying deportment. They are less energetic, less basic, and yield insoluble oxygen and sulphur derivatives; their naturally occurring compounds, as a general thing, have metallic lustre, and are termed *ores*.

Most metals are very *malleable* and *tenacious*, hence can be beaten into thin plates and leaves, and drawn out into wires; gold and silver are the most malleable. A few, like antimony, bismuth, and tin, possess a metalloidal character, are *brittle*, and may be pulverized. Heat will fuse all metals, although some require the high temperature of the oxy-hydrogen flame.

The fusing points of the most important of them are the following:—

Mercury,	—39°	Germanium,	900°
Rubidium,	+38°	Silver,	954°
Potassium,	62°	Gold,	1035°
Sodium,	97°	Copper,	1054°
Tin,	228°	Cast Iron,	1150°
Bismuth,	270°	Wrought Iron,	1500°
Cadmium,	315°	Palladium,	1500°
Lead,	334°	Platinum,	1780°
Zinc,	423°	Iridium,	1950°
Aluminium,	750°		

A greater volatility also corresponds with the greater fusibility. Mercury boils at 360°; potassium and sodium about 440°; cadmium at 860°; zinc toward 1000°, and the difficultly fusible metals may also be volatilized by the galvanic current.

All these physical properties bear a periodic dependence to the atomic weights, as will be more plainly indicated in the individual groups.

SPECIFIC HEAT—ATOMIC HEAT.

Of all physical properties of the elements, from a chemical standpoint, their heat capacity is the most important, as it can serve for the determination of the atomic weights. To heat one and the same quantity, by weight, of the different metals or substances to one and the same temperature, would require very different amounts of heat. This is evident from the following experiments. If we add to 1 kilogram of H_2O at 0° 1 kilogram of H_2O at 100°, the temperature of the mixture of 2 kilograms of water is 50°. The quantity of heat necessary to raise 1 part, by weight, of H_2O, 1°, is almost the same for all temperatures from 0–100°; this is designated the *heat unit* or calorie. On bringing to 1 kilogram H_2O at 0° 1 kilogram Hg at 100°, the temperature of the water and of the mercury after their compensation, will equal only 3.2°. Consequently, the mercury has cooled about 96.8° (from 100 to 3.2°), and given off 3.2 calories. The quantities of heat, contained in equal parts, by weight, of water and mercury, therefore, are as 96.8 to 3.2, *i. e.*, the specific heat of mercury (that of water being made $= 1$) is $\frac{3.2}{96.8} = 0.0332$.

On comparing the specific heats of solid elements found in this way with their atomic weights, we discover that these are inversely proportional to the latter, and hence the product of the specific heat and atomic weight for all solid elements (few excepted) is a constant quantity. This fact was first discovered by Dulong and Petit (1819), and formulated in the following law: *The solid elements possess the same atomic heat.*

In the table on p. 261 are presented the specific heats of the elements in solid condition (as far as they have been determined). W represents the specific heat, A the atomic weight, and the product, $W \times A$, the atomic heat.

From the table, it is evident that the atomic heats of most of the elements lie between 5.0 and 6.8, and equal, upon an average, 6.4.

It is only in the case of a few elements that the atomic heat is somewhat less (S, P, Si, Al, Ge), or considerably less (C, B, Be), than the mean. They are such as have low atomic weight, a metalloidal character, and occupy the middle of the two small periods. These variations bear distinct periodic dependence to the atomic weights:—

Li	Be	B	C	N	O	Fl
6.6	3.8	2.8	1.9	—	—	—
Na	Mg	Al	Si	P	S	Cl
6.7	5.9	5.5	4.6	5.8	5.7	—

Elements.		W	A	W × A
Hydrogen*		5,880	1	5.9
Lithium	Li	0,941	7.6	6.6
Beryllium	Be	0,408	9.1	3.8
Boron (amorphous)	B	0,254	10.9	2.8
Graphite	C	0,174	12	2.1
Diamond		0,143		1.7
Sodium	Na	0,293	23	6.7
Magnesium	Mg	0,245	23.9	5.9
Aluminium	Al	0,202	27.3	5.5
Silicon (cryst.)	Si	0,165	28	4.6
Phosphorus (yellow)	P	0,189	31	5.9
Sulphur (rhombic)	S	0.178	32	5.7
Potassium	K	0,166	39	6.5
Calcium	Ca	0,170	39.9	6.8
Chromium	Cr	0,100	52.4	5.2
Manganese	Mn	0,122	54.8	6.7
Iron	Fe	0,112	55.9	6.3
Cobalt	Co	0,107	58.6	6.3
Nickel	Ni	0,108	58.6	6.4
Copper	Cu	0,093	63.2	5.9
Zinc	Zn	0,093	64.9	6.1
Gallium	Ga	0,079	69.8	5.5
Germanium	Ge	0,057	72.3	5.4
Arsenic (cryst.)	As	0,082	74.9	6.2
Selenium (cryst.)	Se	0,080	78.9	6.4
Bromine (solid)	Br	0,084	79.7	6.7
Zirconium	Zr	0,066	90	6.0
Molybdenum	Mo	0,072	95.8	6.9
Ruthenium	Ru	0,061	103	6.3
Rhodium	Rh	0,058	104	6.0
Palladium	Pd	0,059	106.2	6.3
Silver	Ag	0,056	107.6	6.0
Cadmium	Cd	0,054	111.9	6.0
Indium	In	0,057	113.4	6.5
Tin	Sn	0,054	117.5	6.5
Antimony	Sb	0,052	119.6	6.2
Tellurium	Te	0,047	125	6.0
Iodine	I	0,054	126.5	6.8
Lanthanum	La	0,045	139	6.2
Cerium	Ce	0,045	140	6.2
Didymium	Di	0,045	142	6.5
Tungsten	W	0,033	184	6.1
Osmium	Os	0,031	195	6.2
Iridium	Ir	0,032	192.5	6.3
Platinum	Pt	0,032	194.3	6.4
Gold	Au	0,032	196.2	6.4
Mercury (solid)	Hg	0,032	200	6.4
Thallium	Tl	0,033	203.6	6.8
Lead	Pb	0,031	206.4	6.5
Bismuth	Bi	0,030	207	6.5
Thorium	Th	0,027	232	6.4
Uranium	Ur	0,027	240	6.6

* As Palladium hydride.

The variations from the mean are in part explained by the fact that most of the elements, in their different modifications (crystalline, amorphous, malleable), possess a somewhat different heat capacity, as observed with carbon. The influence of temperature is, however, more important. The figures in the table mostly indicate the heat capacities at medium temperatures. It was known before that these show a slight increase with the temperature, but it is only recently, that H. E. Weber has proved that the increase is very considerable for the elements, C, B and Si, which, at medium temperatures, possess a remarkably low atomic heat; that, beyond a definite temperature, the atomic heat becomes tolerably constant, and then almost agrees with the law of Dulong and Petit. According to Nilson, beryllium shows a similar deportment:—

	W	A	W × A
Diamond, graphite, above 600°	0.459	11.97	5.4
Boron, above 600°	0.5	10.9	5.5
Silicon, above 200°	0.203	28	5.6
Beryllium at 257°	0.58	9.1	5.2

It is probable that there is a definite temperature for all elements, at which their heat capacities can be compared with accuracy.

From this close agreement of the found atomic heat of the metals with the mean, it follows, without doubt, that there does occur a regularity, and we must conclude that the slight variations, apart from the inaccuracy of the observations, are influenced by secondary causes. Hence, the specific heat may serve for the derivation of the atomic weight of the elements; *the atomic weight is equal to the constant quantity*, 6.4 *divided by the found specific heat*:—

$$A = \frac{6.4}{W}.$$

The atomic weights derived from the specific heat—the so-called *thermal atomic weights*—agree in almost all instances with those obtained from the vapor density of the free elements or their volatile compounds. Where no volatile compounds of an element are known, the specific heat is the only certain means of fixing the actual atomic weight. The equivalent weight, 37.8 (InCl), of indium is fixed with great accuracy by analysis; it is, however, unknown whether the atomic weight is double or triple that quantity. The specific heat of indium is 0.0569, from which the atomic weight would be $\frac{6.4}{0.0569} = 112.5$—a number closely approaching the trebled equivalent weight of indium, 113.4 (= 37.8 × 3). From this it follows that the true atomic weight of indium is 113.4 and that indium is trivalent ($InCl_3$).

In their solid compounds the elements retain the specific heat attaching to them in their free, solid state; hence the molecular heat is nearly equal to the sum of the atomic heats of the elements constituting the molecules—law of Neuman and H. Kopp. Hence the atomic heat of elements not known in solid condition may be derived from the molecular heat of their compounds. In this manner the following atomic heats are found: For nitrogen, 5.0; for chlorine, 5.9; for oxygen, 4; for fluorine, 5; for hydrogen, 2.3.

In the free state the gaseous elements usually have a slighter atomic heat, as seen from the following table :—

	A	W*	A×W
Oxygen	16	0.156	2.5
Hydrogen	1.003	2.405	2.4
Nitrogen	14.041	0.172	2.4
Chlorine	35.45	0.093	3.3

The law that the atoms in solid condition possess the same thermal capacity ($A. W. = A.' W.'$), finds an interesting analogy and exemplification in the results derived from the kinetic gas theory, and in the proposition of Avogadro, that the molecules in gas condition, at like temperatures have a similar degree of motion ($M. v. = M'. v'.$), and that the latter experiences like increases. The molecules are the smallest particles for gases, and the atoms the smallest parts of the solid, which possess the same heat energy. The velocity of their heat motion, both for the molecules and the atoms, is, therefore, greater the smaller their masses.

ISOMORPHISM.

As indicated in the preceding pages, the atomic weights of the elements may be derived directly from the heat capacity of solids, while from the gas density of the volatile compounds we get the molecular weights, and from the latter, indirectly, ascertain the atomic weights (compare p. 80). A third, although less general and certain means of determining the atomic and molecular weights is afforded by *isomorphism*. By this is understood the phenomenon observed by Mitscherlich (1819), that bodies chemically similar possess the same or almost the same crystal form. An essential mark of isomorphous bodies is their ability to crystallize together—to form so-called isomorphous mixtures. Conversely

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* By constant volume.

from the isomorphism of two compounds may be concluded an analogous chemical composition, an equal number of atoms in the molecule. This would lead us to accept as relative atomic weights, those quantities of the elements which replace each other in isomorphous compounds. For example, the metals calcium, strontium and barium do not afford volatile derivatives. Their atomic weights could not be deduced from their thermal capacity, and it was the isomorphism of many of their compounds with those of magnesium that determined the same; the quantities of these elements, replacing 24 parts by weight of magnesium (1 atom), were accepted as the true atomic weights.

In the present state of chemistry we attach but secondary importance to isomorphism as a method of determining atomic weights. The phenomena of pleomorphism, according to which one and the same substance frequently possesses several crystalline forms, teach us that the latter are not only dependent upon the chemical molecules, but that these (according to yet unknown laws) may unite to more complicated crystal molecules. Hence, isomorphism affords a means for determining the molecular value of solid substances.

On the other hand we know of many cases where compounds chemically dissimilar possess a similar isomorphous crystalline form. Thus, dimorphous calcium carbonate ($CaCO_3$), as calcite is isomorphous with sodium nitrate (NO_3Na), while as aragonite it is isomorphous with potassium nitrate (KNO_3). Consequently, isomorphism is only to be applied with care in chemical conclusions. Yet it is generally seen that bodies chemically similar have like crystalline forms, especially if the similarity of the elements be taken into consideration according to groups, as expressed in the periodic system. Thus, the isomorphism of the sodium compounds with the silver and cuprous derivatives, of the permanganates with the perchlorates (ClO_4K), of the chromates with the sulphates (SO_4Na_2), confirms the relations presented in the periodic system. Details upon this will be noticed in the consideration of the individual groups.

CHEMICAL PROPERTIES OF THE METALS.

As a usual thing the metals combine, without difficulty, with the metalloids, and with them yield well-characterized compounds, the properties of which are essentially different from the elements composing them. The greater the chemical difference of two bodies (metals and non-metals, bases and acids) the more energetic, in general, is their tendency to unite, and the more different and more stable the resulting products. As we have seen, the analogous metalloids (the groups of chlorine, of sulphur) form derivatives with each other that are not very characteristic. In the same manner when fused together the metals form indefinite metal-like compounds, known as alloys.

Alloys, for the solid condition, are essentially the same as solutions for the liquid. Solutions and alloys constitute the transition from mechanical mixtures to the real chemical compounds. In both instances the constituents possess but a slight affinity for each other, and, therefore, unite in almost all proportions to the so-called *undetermined compounds* (see p. 92). We, however, know that *definite* compounds frequently exist in solutions; thus in an aqueous solution of sulphuric acid there is present the hydrate $H_2SO_4.2H_2O$; in aqueous nitric acid the hydrate $HNO_3.H_2O$. And in the solutions of the salts crystallizing with water of crystallization there are definite compounds with water (*e. g.*, $Na_2SO_4.10H_2O$; $CoCl_2.6H_2O$) at certain temperatures. Similarly constituted combinations appear to be present, also, in the alloys; they often separate in crystalline form after fusion, and represent compounds with definite atomic relations. Antimony and tin form a crystalline compound of the composition Sb_2Sn_3. The crystalline form is always influenced by definite chemical compounds. This double character of the alloys manifests itself in their properties. In many respects they show the average deportment of the metals from which they arise. By combining the various metals we can procure alloys of the desired properties; on this is founded the technical application of the same. Thus, to gold and silver, which are very soft in a pure condition, we can impart a greater hardness by alloying them with copper; and the latter, again, may be rendered harder by fusion with zinc. The character of a chemical compound is exhibited in other properties of the alloys. Their temperature of fusion is generally not the mean of the metals constituting them, but always lies lower. An alloy of 8 parts lead, 15 Bi, 4 Sn and 3 Cd melts at 65°, although each of the single metals fuses above 200°.

Mercury is able to dissolve almost all metals, forming alloys known as *amalgams*, which can crystallize. In chemical respects hydrogen is a metal, but most of the metals do not combine with it, probably because of its volatility. Palladium, potassium and sodium furnish the compounds Pd_2H, K_2H and Na_2H, which deport themselves as alloys, while copper yields a pulverulent compound (CuH). That antimony yields a gaseous product (SbH_3), is due to its pronounced metalloidal character. The ability of individual metals of the platinum and iron group to permit the passage of hydrogen at a red heat depends, probably, upon a chemical attraction; hydrogen first dissolves and is then evaporated again.

Halogen Compounds.—The metals unite directly with the halogens to form salt-like compounds, which are not decomposed by water at ordinary temperatures, and, in general, are very stable; on the other hand, the halogen compounds of the metalloids (excepting those of carbon) are easily broken up by water. These compounds are also produced by the action of the haloid acids upon the free metals, their oxides, hydroxides, and carbonates, whereby they plainly characterize themselves as salts of the haloid acids. A third procedure for the formation of chlorides and bromides, essentially analogous to the first, is based upon the simultaneous action of carbon and chlorine, or bromine upon the oxides (see Chloride of Aluminium and Silicon).

The following types of halogen derivatives exist and show the different valences of the metals:—

$$\overset{\text{I}}{K}Cl \quad \overset{\text{II}}{Zn}Cl_2 \quad \overset{\text{III}}{In}Cl_3 \quad \overset{\text{IV}}{Sn}Cl_4 \quad \overset{\text{V}}{Ta}Cl_5 \quad \overset{\text{VI}}{W}Cl_6.$$

The higher valence of the elements is more manifest in their more stable oxygen compounds.

OXIDES AND HYDROXIDES—HYDRATES.

The affinity of the metals for oxygen varies. Some of them oxidize in moist air and decompose water, even at ordinary temperatures. Such are the so-called alkalies and alkaline earths (the potassium and calcium groups). Their oxides dissolve readily in water and form strong basic hydroxides or hydrates (KOH, $Ca(OH)_2$), which are usually not decomposed by ignition. Other metals (the so-called heavy metals) oxidize and decompose water only at higher temperatures; their oxides are insoluble in water, and generally afford no hydroxides, as the latter upon heating readily decompose into oxides (anhydrides) and water:—

$$Zn(OH)_2 = ZnO + H_2O.$$

They are of a less basic nature, and their soluble salts usually exhibit acid reaction. Some metals, finally, as gold and platinum (the noble metals), are incapable of combining directly with oxygen. Their oxides, obtained in another way, decompose readily under the influence of heat into metal and oxygen. The universal method for the preparation of insoluble oxides and hydroxides of the heavy metals depends upon the precipitation of the solutions of their salts by alkaline bases :—

$$\overset{II}{Cu}SO_4 + 2KOH = K_2SO_4 + \overset{II}{Cu}(OH)_2.$$

The different valence of the metals is most clearly seen in their oxygen derivatives, that form salts. We have the following eight forms or types of the highest salt producing oxides (see p. 252), corresponding to the eight groups of the periodic system of the elements :—

$$\overset{I}{K_2}O \quad \overset{II}{Mg}O \quad \overset{III}{Al_2}O_3 \quad \overset{IV}{Sn}O_2 \quad \overset{V}{Bi_2}O_5 \quad \overset{VI}{Cr}O_3 \quad (\overset{VII}{Mn_2}O_7) \quad \overset{VIII}{Os}O_4.$$

These correspond to the hydroxides or hydrates :—

$$\overset{I}{K}OH, \quad \overset{II}{Mg}(OH)_2 \quad \overset{III}{Al}(OH)_3 \quad \overset{IV}{Sn}(OH)_4 \quad \overset{V}{Bi}(OH)_5 \quad \overset{VI}{Cr}(OH)_6 \quad \overset{VII}{Mn}(OH)_7.$$

The oxides and hydroxides of the first two forms possess a strong basic character and only furnish salts with acids. In the oxides and hydroxides of the succeeding forms there is shown an acid-like character together with the predominating basic character. Hence they dissolve in alkalies and form salt-like derivatives with bases, in which hydrogen is replaced by metals, *e.g.*, $Al(ONa)_3$. These higher (normal) hydrates are not very stable, give up water and pass into *meta-hydrates*, which retain the acid character. Thus, from $Al(OH)_3$ is derived $AlO.OH$, which yields salt-like compounds, *e.g.*, $AlO.OK$; from $Sn(OH)_4$ are derived stannic acid, $SnO(OH)_2$, and its salts, as SnO_3K_2. Finally, the oxides of the last three groups are only of an acid nature, and afford salts with bases. The corresponding highest hydroxides are very unstable or do not exist; inasmuch as they yield the ordinary acids (p. 253) by the elimination of one, two and three molecules of water :—

$\overset{V}{Bi}O_3H$	$\overset{VI}{Cr}O_4H_2$	$\overset{VII}{Mn}O_4H$
Bismuthic acid.	Chromic acid.	Permanganic acid.
HNO_3	SO_4H_2	$ClO_4H.$
Nitric acid.	Sulphuric acid.	Perchloric acid.

Like the metalloids, the metals of the last four series form lower oxides and hydrates (p. 252) in which they exhibit a lower valence :—

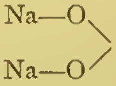
$$\overset{II}{Sn}(OH)_2, \quad \overset{III}{Bi}(OH)_3, \quad \overset{IV}{Mo}(OH)_4, \quad \overset{II}{Mn}(OH)_2.$$

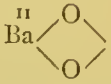
These lower oxides have a basic character, and it is the more pronounced the further removed they are from the limiting form. In their whole deportment they resemble the corresponding combination forms of the metals of the first three groups.

The metals of the first two groups have higher oxygen compounds, called *peroxides*, *e. g.*, Na_2O_2, BaO_2. These do not form corresponding salts, and readily lose an atom of oxygen. By the action of dilute acids hydrogen peroxide is produced :—

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2.$$

In consequence of this reaction, it is very probable that in the peroxides, the oxygen atoms are arranged in a chain-like manner as in hydrogen peroxide :—





When concentrated acid acts upon them, oxygen is evolved, and salts of the lower oxides result; heated with hydrochloric acid, chlorine is generated :—

$$BaO_2 + 4HCl = BaCl_2 + 2H_2O + Cl_2.$$

Ordinarily, all higher oxides which are not able to form salts and which evolve chlorine with hydrochloric acid are termed peroxides, *e.g.*, PbO_2, lead peroxide, and MnO_2, manganese peroxide. However, these latter compounds do not possess the structure of true peroxides. Lead dioxide, PbO_2, is wholly analogous to tin dioxide, $\overset{IV}{Sn}O_2$, and is capable of combining with bases; therefore we must grant in it a direct union of the two oxygen atoms with tetravalent lead. So manganese is probably tetravalent in manganese peroxide. The difference between these oxygen compounds and the true peroxides is shown by their inability to form hydrogen peroxide. This behavior finds an explanation in the thermochemical relations, inasmuch as it is only the true peroxides that, by action of acids, disengage sufficient heat to allow of the production of hydrogen peroxide.

Finally, some monovalent metals are capable of forming oxides containing four atoms of metal, *e. g.*, K_4O, Ag_4O ; these compounds are termed *quadrant oxides* or *suboxides.*

Salts.—By the action of bases upon acids, salts and water result :—

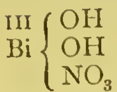
$$NaOH + NO_3H = NO_3Na + H_2O.$$

These are also produced by the direct union of basic with acid oxides : $Na_2O + SO_3 = Na_2SO_4$; and by the action of metals upon the acids. Hence the salts are usually viewed as acids in which hydrogen is replaced by metals. Upon inquiring, however, into the composition of salts we discover them so constituted that a divalent oxygen atom connects the metal with the acid radical (p. 178) :—

$K—O—H$	$K—O—NO_2$	$H—O—NO_2$
Potassium hydroxide.	Potassium nitrate.	Nitric acid.

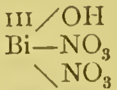
The salts, therefore, according as it is more practicable, can be regarded as acid derivatives, and also as derived from the basic hydroxides by replacement of hydrogen.

As we have seen, the polybasic acids yield the *primary*, *secondary*, *tertiary*, *etc.*, *salts* by the replacement of one or several hydrogen atoms. In the same manner primary, secondary, etc., salts are derived from polyvalent metals (or the polyacid, polyhydric bases):—

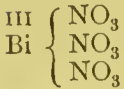


$$\overset{\text{III}}{\text{Bi}}\begin{cases}\text{OH}\\ \text{OH}\\ \text{NO}_3\end{cases}$$

Primary bismuth nitrate.



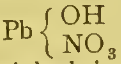
Secondary bismuth nitrate.



$$\overset{\text{III}}{\text{Bi}}\begin{cases}\text{NO}_3\\ \text{NO}_3\\ \text{NO}_3\end{cases}$$

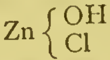
Tertiary bismuth nitrate.

Such salts in which not all the hydroxyl groups of the polyacid hydroxide are replaced by acid residues are called *basic* :—



$$\text{Pb}\begin{cases}\text{OH}\\ \text{NO}_3\end{cases}$$

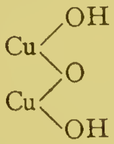
Basic lead nitrate.

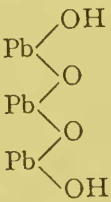


$$\text{Zn}\begin{cases}\text{OH}\\ \text{Cl}\end{cases}$$

Basic zinc chloride.

Besides these basic salts there exist some of another form. We saw that the polybasic acids can combine to form poly- or anhydro-acids; similarly, the polyhydric bases form polyhydrates:—



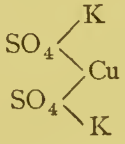


from which basic salts are obtained (see copper and lead) by replacement of hydroxides by acid residues.

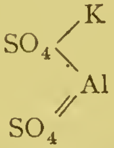
By the replacement of the hydrogen atoms in the polyhydric acids or bases by various radicals we get the so-called mixed or *double salts* :—

$$\text{PO}_4\begin{cases}\text{K}\\ \text{NH}_4\\ \text{H}\end{cases}$$

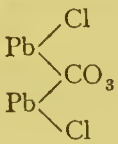
Pot. am. phosphate.

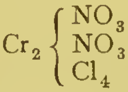


Pot. copper sulphate.



Pot. aluminium sulphate.





$$\text{Cr}_2\begin{cases}\text{NO}_3\\ \text{NO}_3\\ \text{Cl}_4\end{cases}$$

The halogen double salts are usually viewed as molecular compounds :—

$MgCl_2.KCl$ $AuCl_3.KCl$ $PtCl_4.2KCl$.

If, however, the fluorides of boron and silicon, $BFl_3.KFl$, $SiFl_4.2KFl$, are derived from peculiarly constituted atomic acids, $HBFl_4$, H_2SiFl_6, then a peculiar union of atoms may be regarded as existing in the metallic double chlorides,* which are often very similar and isomorphous.

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* Consult *American Chemical Journal*, 11, p. 291.

ACTION OF METALS UPON SALTS AND ACIDS.

We have seen that the metals by solution in acids are able to form salts. In this case the hydrogen is directly replaced by the metal and separated in free condition (providing in the moment of its formation it does not act upon the acids):—

$$Zn + SO_4H_2 = ZnSO_4 + H_2.$$

The metals deport themselves in the same manner with the salts. Zinc introduced into a solution of copper sulphate is dissolved tc sulphate and metallic copper deposits:—

$$Zn + CuSO_4 = ZnSO_4 + Cu.$$

Herein is shown the perfect analogy between acids and salts. In chemical nature hydrogen is a metal. Hence the acids may be viewed as hydrogen salts: *hydrogen sulphate* for sulphuric acid, *hydrogen nitrate* for nitric acid, etc. The similarity of salts and acids shows itself, too, in their acidity. All soluble salts of the metals, whose hydroxides are weak bases, exhibit acid reaction, and color blue litmus paper red. Only the salts of the strong basic metals, like potassium and calcium, show a neutral or basic reaction—providing the base is stronger than the acid.

The displacement of metals from their salts by others, was formerly regarded as exclusively influenced by their electrical deportment. Indeed the more electro-positive, basic metals replace the electro-negative, less basic. In the following series each metal throws out from solution those preceding it: Au, Pt, Ag, Hg, Cu, Pb, Sn (Fe, Zn). Iron and zinc precipitate almost all the heavy metals from solutions of their salts. The strongly positive potassium is able to displace all other metals. This is very evident from the action of molten potassium upon the haloid salts—a reaction which frequently serves for the separation of the metals in a free condition:—

$$AlCl_3 + 3K = Al + 3KCl.$$

In its electrical deportment hydrogen stands near zinc; like the latter, it must, therefore, displace all more negative metals. If this does not happen, the cause must be sought in its volatility; in fact, we know that hydrogen, under pressure, is capable of separating gold, silver and some other metals from their salt solutions.

Formerly great importance was attributed to the electrical behavior of the elements, and all were arranged in an electro-chemical series, in which oxygen figured as the most negative and potassium as the most positive member—$\overset{-}{O} \ldots\ldots \overset{+}{K}$. The opinion prevailed that the chemical affinity of the elements depended upon their electrical differences, and that chemical union occurred because the opposite electricities united—*electro-chemical theory* of Berzelius. Now, however, we know that in the expression of chemical affinity only secondary importance is attached to the electrical deportment of bodies. Although the affinity, in general, corresponds to the electrical difference, yet this does not always occur. Thus, the strongly negative chlorine expels bromine and iodine from their hydrogen, and nearly all their metallic compounds; however, chlorine and bromine are conversely displaced by iodine from their oxygen compounds (ClO_3H and ClO_4H) (p. 186). Similarly, lead separates tin from its chloride, $SnCl_4$, while, on the other hand, tin throws out lead from the solution of its oxides in alkalies.

At present, it is established that the mutual deportment of the metals is dependent upon and regulated by their thermo chemical relations. A metal displaces another from its oxygen salts, as well as from its oxides, sulphides, or halogen compounds, if the heat of formation of the resulting bodies is greater than that of those acting; this agrees with the principle of greatest heat development. Thus, copper displaces silver from its sulphate, because the heat of formation of the copper sulphate (in aqueous solution) is about 33.5 calories greater than that of silver sulphate. Sulphuric acid dissolves most metals with liberation of hydrogen, because their heat of formation,

$$(S,O_4,H_2) = 192.9 \quad (S,O_4,H_2,Aq.) = 210.7,$$

is less than that of most of the sulphates. The heat of formation of lead sulphate (Pb,S,O_4) equals 213 5; therefore, lead would be dissolved by dilute sulphuric acid, did not the insolubility of lead sulphate in the dilute acid prevent it from so doing. Concentrated sulphuric acid, on the other hand, does dissolve lead, because lead sulphate is soluble in it. For the same reason, potassium displaces almost all the other metals; on the other hand, potassium is separated by sodium amalgam, with formation of potassium amalgam, as the heat of formation of the latter is much greater than that of sodium amalgam, and therefore, in the equation,

$$(K,Cl) + (Na,Hg) = (Na,Cl) + (K,Hg),$$

the thermal value upon the right side overbalances. (Berthollet.)

Although the affinity relations dependent upon the quantity of heat frequently correspond with the electrical differences of the free elements, this is so influenced that the electro-motive energy is induced by the heat, and is proportional to the same (see p. 274). The heat of formation of the compounds constitutes the primary cause of their chemical transposition; it varies in the different compounds for the same element, and thus explains the opposing deportment of the elements. Chlorine displaces iodine in iodides, not because it is more strongly electro-negative, but because the heat of formation of the chlorides is greater than that of the iodides. Conversely, chlorine is eliminated from chloric acid by iodine, because the heat of formation of the iodic acid is the greater (compare p. 186). H_2S and I, are similarly transposed, in the presence of water, into HI and sulphur, while iodine is separated from concentrated hydriodic acid by boiling with sulphur (p. 67).

ELECTROLYSIS OF SALTS.

On subjecting a salt in a fused or dissolved condition to the action of an electric current, it is decomposed, so that the metal separates upon the negative pole and the acid group or halogen upon the positive:—

$$NaCl = \overset{+}{Na} + \overset{-}{Cl}.$$

The oxygen salts behave in the same way; the metal upon the negative pole, the acid residue upon the positive:—

$$CuSO_4 = \overset{+}{Cu} + \overset{-}{SO_4}.$$

As the liberated acid residue cannot exist in a free condition, a secondary reaction occurs, by which it generally, especially in the electrolysis of aqueous solutions, breaks up into oxygen and an acid oxide, which, with the water of the solution, again forms the acid:—

$$SO_4 + H_2O = SO_4H_2 + O.$$

Thus, in the electrolysis of salts, the metal and oxygen separate out—the first at the negative, the latter at the positive pole. That the decomposition, indeed, occurs in the manner indicated is confirmed by the fact that the free acid arises at the positive pole.

All neutral salts are similarly decomposed. If, however, the metal contained in the salt acts upon water when free, manifestly a secondary reaction must occur at the negative pole. The real electrolytic decomposition of potassium sulphate would then take place according to the following equation:—

$$SO_4K_2 = \overset{+}{K_2} + \overset{-}{(SO_3 + O)}.$$

The separated potassium decomposes the water with formation of potassium hydroxide and the disengagement of hydrogen:—

$$K + HOH = KOH + H.$$

Therefore, hydrogen and potassium hydroxide occur as definite decomposition products, at the negative pole; at the positive, however, we have oxygen and sulphuric acid. On coloring the liquid exposed to the electrolysis with a little violet syrup, that part at the + pole will become red, owing to the acid formed, while that at the — pole will have a green color from the base. That the electrolytic decomposition of potassium sulphate and similar salts proceeds in the manner given, may be proved experimentally by using mercury as negative electrode; then the separated potassium will combine with the mercury and form an amalgam, which will act gradually upon the water.

It was formerly believed that the alkali salts were directly decomposed by electrolysis into metallic and acid oxides, which yielded the hydrates (KOH and SO_4H_2) with water; the appearance of H and O was attributed to the simultaneous electrolytic decomposition of water (a view which was set aside by the behavior of the other salts). With this erroneous idea as a basis, all salts were held to be binary compounds of the metallic oxides (bases) with acid oxides (acids), *e. g.*, $K_2O.SO_3 = K_2SO_4$, $K_2O.N_2O_5 = 2KNO_3$ — dualistic theory of Berzelius. The acids and bases were also thought to be binary compounds of a metallic oxide or acid anhydride with water :—

$$K_2O.H_2O = 2KOH. \quad SO_3.H_2O = H_2SO_4.$$

The acid oxides or anhydrides were termed acids and the true acids hydrates.

Other compounds are decomposed in the same way as the salts. Thus, molten caustic potash, KOH, breaks up into K and OH; the first separates in metallic form upon the negative pole (and gradually acts upon KOH with hydrogen disengagement), while at the positive pole water and oxygen appear—produced by decomposition of the hydrogen peroxide formed at first :—

$$(OH)_2 = H_2O + O.$$

Acids sustain decompositions similar to those of salts. They are, indeed, nothing more than hydrogen salts. Hydrochloric acid, for example, breaks down into hydrogen and chlorine. Sulphuric acid, H_2SO_4, is decomposed in aqueous solution into the ions 2H and SO_4 or H and SO_4H. The anion SO_4 (or SO_4H) is immediately converted by the water into sulphuric acid and oxygen: $SO_4 + OH_2 = SO_4H_2 + O$. The final decomposition products are, therefore, hydrogen and oxygen. Sulphur heptoxide, S_2O_7 : $2SO_4 = S_2O_7 + O$, is formed in minute quantities.

It is, therefore, probable that the water is also decomposed in an analogous manner :—

$$2HOH = H_2 + O_2H_2;$$

the peroxide produced at first breaks up, however, for the most part, into water and oxygen.

Considering the quantities which are deposited from various compounds by the same electric current, we will discover that *a like number of valences are invariably dissolved in like time, i. e.*, equivalent quantities are separated according to the idea of the valence theory (p. 171). (The law of Faraday and Becquerel.) Thus in the simultaneous decomposition of hydrochloric acid, water and ammonia (pp. 74, 99, 130), equal volumes of hydrogen (= 1 part) are liberated, while at the positive pole 1 volume of chlorine (= 35.45 parts), ½ volume of oxygen (= 8 parts) and ⅓ volume of nitrogen (= 4.67 parts) appear. The quantities decomposed by electrolysis, therefore, bear the ratio :—

$$HCl, \ \frac{H_2O}{2}, \ \frac{H_3N}{3}.$$

In the same way, equal quantities of chlorine are set free from all metallic chlorides (and other salts, as the chlorine atoms are alike in all), while the quantities of the precipitated metals agree with the values according to which they enter chemical action. The quantities of the different salts, decomposed by electrolysis, stand in the following relation :—

$$AgNO_3, \frac{CuCl_2}{2}, \frac{Cu_2Cl_2}{2}, \frac{SbCl_3}{3}, \frac{Fe_2Cl_6}{6}, \frac{SnCl_4}{4}, \frac{HgCl_2}{2}, \frac{Hg_2(NO_3)_2}{2}.$$

Therefore, 31.8 parts Cu are deposited for the 35.4 parts Cl in cupric chloride ($Cu''Cl_2$), but from cuprous chloride ($Cu'Cl$) we obtain 63.6 parts Cu; from mercuric chloride ($Hg''Cl_2$) we obtain 100.2 parts Hg, and from mercurous nitrate ($Hg'NO_3$) 200 parts Hg, etc. The quantities of the metals existing in the different states of oxidation, and which are equivalent to each other, vary and correspond to their chemical affinity. Like valences are dissolved in equal periods of time.

As the quantity of heat liberated in the union of like valences (in KCl, CuCl, $AgNO_3$, etc.), and that necessary for the decomposition are very different, and since Faraday's law calls for the solution of like valences in equal periods by the same current—the performance of a different amount of work—there must occur, in consequence of the law of the conservation of energy (if the electric current does indeed do the electrolytic work), an unequal distribution of the energy of the current upon the different electrolytes. The manner of this distribution is not known. Faraday thought it probably took place in such a manner that the greater consumption of energy by the electrolytes was compensated by their resistance, which, consequently, is so much less.

The relation of the electro-motive force of a galvanic cell to the chemical transposition occurring within it is equally obscure. Disregarding the electric contact theory, the source of the former (with the principle of the conservation of energy as basis) can only be found in the loss of chemical energy (heat disengagement), which corresponds to the change taking place within the galvanic element. Following the experiments of Joule and others, W. Thomson assumed that the energy, developed by a cell, was proportional or equal to (providing no secondary actions occurred) the thermal value of the chemical reaction producing it. Thus, the effectiveness of a Daniell element (combination of zinc and dilute sulphuric acid, or zinc sulphate and copper in a solution of copper sulphate) depended on the replacement of Cu in $CuSO_4$ by Zn—a reaction in which 50.1 calories are developed. Further, the action of a Bunsen cell (zinc and carbon in a solution of potassium bichromate and sulphuric acid) was supposed to be due to the formation of zinc and chromium sulphates, in which instance 99.8 calories are set free. In all such constant batteries J. Thomson and others concluded that the electro-motive force is equal or proportional to the energy developed in the chemical reaction. According to a later theory of Helmholtz, and the determinations made by F. Braun, chemical energy cannot be completely, but only partly, transformed into electric energy, just as heat cannot be completely changed to mechanical work. Hence, the electro-motive force of an element is usually less, but should be greater than the heat energy corresponding to the chemical transposition. In the latter cases, we must renounce any relation of the electromotive force to the thermal value, in case these, as is probably true, cannot be explained by secondary chemical reactions which have gone unconsidered heretofore.

Helmholtz asserts that the entire chemical energy is only completely converted into electric energy when the electro-motive force of the element is independent of the temperature. If the electro-motive force increases with the temperature, then heat is developed in addition to the chemical energy, and is withdrawn from the element. In such cases the electro-motive force is greater than the heat value of the chemical transposition. Jahn has confirmed these statements by very recent experiments.

When two salts in solution or fusion come together, a chemical action will frequently occur. Berthollet endeavored (close of preceding century) to explain the resulting phenomena by referring them to purely physical causes, and excluded every special chemical affinity.

In the opinion of Berthollet, four salts always arise in the solution of two. For example, on mixing solutions of copper sulphate and sodium chloride, there exist in solution copper sulphate, sodium sulphate, copper chloride, and sodium chloride:—

$$2CuSO_4 + 4NaCl \text{ yield}$$
$$CuSO_4 + Na_2SO_4 + CuCl_2 + 2NaCl.$$

That copper chloride is really present in the solution together with the sulphate, follows, from the fact that the blue color of the latter acquires a greenish color, peculiar to the copper chloride, by the addition of sodium chloride; other phenomena are not noticeable at first. Suppose one of the four salts formed in the solution is insoluble or volatile, the reaction will occur somewhat differently. Upon adding barium chloride to the copper sulphate solution four salts will be formed at the beginning just as in the first case. The barium sulphate produced separates, however, in consequence of its insolubility, the equilibrium of the four salts will be disturbed, and new quantities of $CuSO_4$ and $BaCl_2$ act upon each other until the transposition is complete:—

$$CuSO_4 + BaCl_2 = BaSO_4 + CuCl_2.$$

The chemical transposition may, therefore, be explained by the insolubility of the barium sulphate. On adding HCl, or soluble chlorides, to the solution of a silver salt all the silver is precipitated as chloride, because the latter is insoluble.

Take another example. On adding sulphuric acid to a solution of potassium nitrate there is apparently no perceptible alteration. We may suppose that the four compounds, KNO_3, K_2SO_4, H_2SO_4 and HNO_3, are present in the solution. Upon warming the latter volatile nitric acid will evaporate, and, in proportion to its separation, new quantities of potassium nitrate and hydrogen sulphate will act upon each other until the transposition is complete:—

$$2KNO_3 + H_2SO_4 = K_2SO_4 + 2HNO_3.$$

The decomposition of potassium nitrate by sulphuric acid occurs, therefore, in consequence of the volatility of the nitric acid. Sulphuric acid decomposes sodium chloride in the cold, because hydrogen chloride is volatile. Carbonates are even decomposed by very weak acids, because the carbonic acid, H_2CO_3, at once separates gaseous carbon dioxide, CO_2.

In many instances the chemical transpositions may be explained by such physical causes, and there is no doubt that an important rôle attaches to them. It is, however, not justifiable to ignore any special chemical affinity between the various substances, as did Berthollet. Irrespective of all physical causes, the reactions are determined by chemical affinity. This is seen in the solutions of salts. Mix, *e. g.*, ferric chloride with potassium acetate, and there is obtained a dark-red solution, in consequence of the formation of iron acetate. Although an insoluble salt is not produced here, yet the rearrangement of the two salts, evident from the optical properties of the solution, is a perfect one; only iron acetate and potassium chloride are present in the solution:—

$$Fe_2Cl_6 + \underset{\text{Pot. acetate.}}{6C_2H_3O_2K} = (C_2H_3O_2)_6Fe_2 + 6KCl.$$

The transposition is determined by the strong affinity of potassium for chlorine and by the weak basic nature of the ferric oxide. If the difference between the affinities of the bases and salts is not so great, then four salts can exist in solution; their quantity, however, will be proportional to the different affinities and determined by the equilibrium of all the forces of attraction. Thus four salts are present in the previously mentioned solution of copper sulphate and sodium chloride, the quantities of copper chloride and sodium sulphate are, however, much greater than those of copper sulphate and sodium chloride (proved by the optical properties of the solution), because the affinity of sulphuric acid for sodium is greater than the same for copper.

The phenomena recorded above are the subject of controversy and many investigations at the present time. Generally the chemical transpositions of salts with salts or with acids (hydrogen salts) and bases, are determined and governed by the tendency (Bestreben) toward the greatest heat disengagement. This is true, too, of other chemical reactions (the precipitation of metals from their salts by other metals, the action of metals upon acids and water, the alternating deportment of metalloids, etc.). In most cases the reaction corresponding to a chemical equation is easier and more complete, the more the sum of the heats of formation of the resulting bodies exceeds that of those reacting (the chemical energy of the first is less than that of the latter). The reverse of the reaction can only succeed by the consumption of energy and requires addition of heat or electricity. This is of practical importance (see Magnesium Chloride) in the review of the details of chemical reactions. In the action of salts and acids these relations are, however, complicated because many reactions, especially in aqueous solution, occur accompanied by a direct absorption of heat. The aim of thermo-chemistry, in accord with the efforts of Berthollet, is to classify such reactions under the principle of the greatest heat disengagement, and declare its exceptions due to the influence of secondary causes. This would bring into consideration the formation of acid and double salts, the influence of the heat of solution, the decomposition of salts by solvents, etc. In this manner very many of the apparent exceptions have been satisfactorily accounted for. However, it is very evident, that the principle of greatest heat-development cannot have an unlimited value, and that all reactions are not of the class in which heat is set free, but that chemical transpositions can also proceed even when heat is absorbed. The decomposition (dissociation) of elements and compounds opposes their tendency to unite, and in such instances heat disappears as such, passing then into chemical energy. In most cases the greater heat formation of compounds argues for a greater stability, yet many compounds are known which have been produced with the liberation of much heat, but are themselves very unstable. In such cases the formation of the most stable derivative prevails, although it does possess the lowest heat of formation. The transpositions then follow with heat absorption in a direction directly opposite that presented by the principle of greatest heat disengagement. Thus, *e.g.*, the heat of formation of water is greater than that of an equivalent quantity of hydrogen chloride :—

$$(H_2,O) \text{ vapor} = 57.2 \text{ Cal.} \quad 2(H,Cl) = 44.0 \text{ Cal.}$$

Yet the latter is more stable than the former. The dissociation of water commences about 1000°, while that of HCl begins at 1500°. Consequently, with a mixture of hydrogen, chlorine and oxygen (in equivalent quantities), if the reaction be induced by application of heat or by the electric spark, the product will be hydrogen chloride exclusively and not water. Again, in a mixture of steam and chlorine, exposed to a temperature of about 1000°, a transposition will occur with heat absorption and result in the production of hydrogen chloride and oxygen.

Heat is not the only agent which causes the decomposition of bodies; many salts undergo changes in water and other solvents, quite analogous to that of dissociation, and the extent of these changes is not always limited to the heat of formation of the component elements. This accounts for the fact that very often transpositions occurring in dilute solutions are accompanied by the absorption of heat.

It is therefore plain that the principle of the greatest heat development is subject to a limitation, conditioned by the stability of the compounds (p. 30).

GROUP OF THE ALKALI METALS.

Potassium,	39.14	Lithium,	7.03
Rubidium,	85.4	Sodium,	23.06
Cæsium,	132.9	(Ammonium).	

The metals of this group are decidedly the most pronounced in metallo-basic character, and this constitutes a visible contrast with the elements of the chlorine group, the most energetic among the non-metals. This contradictory character of both groups is seen, too, in their monovalence: in their combinations with each other, they saturate their affinity by single atoms. The more distinct the chemical character of two elements and the more unlike they are, the simpler and the more definite will the expressions of valence in general be between them.

The alkali metals in physical and chemical properties exhibit great similarity. They oxidize readily in the air, decompose water violently, even in the cold, with the formation of strong basic hydroxides, which dissolve readily in water and are called *alkalies* (caustic potash, caustic soda),—hence the name alkali metal. They are not decomposed by ignition. Their chemical energy increases with increasing atomic weight (more correctly atomic volume, p. 258), sodium is more energetic than lithium, potassium more than sodium, and rubidium more than potassium. Cæsium has not been studied in a free condition, but, judging from its compounds, it possesses a more basic character than rubidium. We saw in other analogous groups (of chlorine, oxygen, phosphorus, carbon), that the metalloidal, negative character diminishes, and the basic increases with the increasing atomic weight.

The atomic weights increase simultaneously with the specific gravities; but as the increase of the former is greater than that of the latter, the atomic volumes (the quotients $\frac{A}{\text{sp. gr.}}$, p. 258), are always the greater. The increasing fusibility and volatility correspond to the increase of the atomic volumes; rubidium distils at a red heat, while lithium only volatilizes with difficulty:—

	Li	Na	K	Rb	Cs
Atomic weight	7.03	23.06	39.03	85.4	132.9
Specific gravity	0.59	0.97	0.86	1.52	1.85
Atomic volume	11.9	23.7	45.4	56.1	71.7
Fusion temperature	180°	95.6°	62.5°	38.5°	26.5°

Although all the alkali metals exhibit a great similarity in their chemical deportment, we discover more marked relations between potassium, rubidium and cæsium upon the one hand, and lithium and sodium on the other, which accords with their position in the periodic system of the elements. Especially is this noticed in the salts. The first three metals form difficultly soluble tartrates and chlorplatinates (see Platinum). Their carbonates deliquesce in the air, while those of sodium and lithium are stable under similar circumstances; the last is, indeed, rather insoluble in water. The phosphates deport themselves similarly; lithium phosphate is very difficultly soluble. It must be remarked that the normal carbonates and phosphates of all other metals are insoluble. In lithium, then, which possesses the lowest atomic weight, it would seem the alkaline character has not yet reached expression, and it in many respects approaches the elements of the second group, especially magnesium, just as beryllium approaches aluminium; this is indicated by the position of the elements in the table, p. 249. The elements of the two small periods are, indeed, similar, but not completely analogous, while the homology of the three great periods finds expression in K, Rb, Cs. See further p. 255.

The affinity relations of the alkalies are expressed and explained by their thermochemical relations. Generally the heat liberation is greater as the atomic weights increase: thus, *e.g.*, in the formation of the chlorides and hydroxides:—

(Li,Cl) = 93.8
(Na,Cl) = 97.7
(K,Cl) = 105.6
(Na_2,O) = 100.2
(K_2,O) = 97.1

(Li,Cl,Aq.) = 102.2
(Na,Cl,Aq.) = 91.5
(K,Cl,Aq.) = 101.1
$(Na_2,O,Aq.)$ = 155.2
$(K_2,O,Aq.)$ = 164.5

(Li,O,H,Aq.) = 117.4
(Na,O,H,Aq.) = 111.8
(K,O,H,Aq.) = 116.4
(Na,O.H) = 102.0
(K,O,H) = 103.9

The position of lithium in the periodic system explains the varying deportment of its compounds, which frequently show a greater heat disengagement than those of sodium. Again, it is very probable that a constant increase in the heat modulus occurs with the true homologues of potassium—rubidium and cæsium.

On the basis of the principle of the greatest evolution of heat, the numbers above would explain why sodium and lithium are displaced from their chlorides, etc., by potassium. It separates most other metals because the heat of formation of the potassium compounds is generally much greater (see p. **271**). On comparing the heat of formation of water (H_2O = 68.6 calories), we immediately perceive why it is so readily decomposed by the alkali metals. All metals, disengaging more than 68.6 calories in the formation of their oxides, Me_2O, or their hydroxides, MeOH, decompose water, and the energy will be greater, the greater the difference of heat. The insolubility of the oxides constitutes an obstacle to the action; this, however, may be removed (see Aluminium) by addition of neutral solvents. Conversely, all oxides, affording less heat in their formation, are reduced by hydrogen.

POTASSIUM.

K = 39.14.

In nature, potassium is found principally in silicates, viz.: feldspar and mica. By the disintegration of these frequently occurring minerals, potassium passes into the soil, and is absorbed by plants; the ashes of the latter consist chiefly of different potassium salts. The chloride and sulphate are also found in sea water, and in large deposits in Stassfurt, at Magdeburg, and in Galicia, where they were left by the evaporation of the water of inclosed seas. Metallic potassium was first obtained by Davy, in the year 1807, by the decomposition of the hydroxide, by means of a strong galvanic current. At present it is prepared by igniting an intimate mixture of carbon and potassium carbonate:—

$$K_2CO_3 + 2C = 2K + 3CO.$$

For demonstration purposes potassium can be prepared by heating a mixture of dry potassium carbonate (1 mol.) and magnesium powder (3 ats.) in a porcelain boat placed in a combustion tube in an atmosphere of hydrogen. The potassium volatilizes and forms a brilliant metallic mirror upon the tube.

Such a mixture may be made by the carbonization of organic potassium salts, *e. g.*, crude tartar. It is then ignited to white heat, in an iron retort, and the escaping potassium vapors collected in receivers of peculiar construction, filled with rock oil. The latter, an hydrocarbon, serves as the best means of preserving potassium, which would otherwise oxidize in the air, and decompose other liquids. In a fresh section, potassium shows a silver-white color and brilliant metallic lustre. At ordinary temperatures it is soft, like wax, and may be easily cut. It crystallizes in octahedra, and has a specific gravity = 0.86. It melts at 62.5° C., and when raised to a red heat, is converted into a greenish vapor. It oxidizes in the air, and becomes dull in color; heated, it burns with a violet flame. It decomposes water energetically, with formation of potassium hydroxide and the liberation of hydrogen. If a piece of the metal be thrown upon water, it will swim on the surface with a rotary motion; so much heat is disengaged by the reaction that the generated hydrogen and the potassium inflame. Finally, a slight explosion usually results, whereby pieces of potassium are tossed here and there; it is advisable, therefore, to execute the experiment in a tall beaker glass, covered with a glass plate. Potassium combines directly and very energetically with the halogens.

On conducting hydrogen over metallic potassium heated to 300°–400°, potassium hydride, K_2H, results. This is a metallic, shining, brittle compound, which, upon stronger heating (410°), more readily *in vacuo*, is again decomposed. Exposed to air, it ignites spontaneously. The sodium hydride, Na_2H, obtained in the same way, does not possess this latter property.

The influence of heat and pressure in the formation and decomposition of these compounds is very noteworthy (p. 96). If, for example, potassium hydride be heated it melts, but otherwise remains unchanged. Above 200° (in a vacuum) it sustains a partial decomposition (dissociation), which gradually increases as the temperature rises. If the heating should take place in a closed vessel provided with a manometer, it will be observed that the decomposition at a given temperature will continue until the liberated hydrogen has acquired a definite tension—until it exerts a definite pressure. For potassium hydride, this tension, at 330° C., equals 45 mm. The decomposition will then cease, but will proceed further at the same temperature if the hydrogen gas be removed, until the pressure of 45 mm. is again reached. In this manner a complete decomposition of the hydride may be effected at the temperature given above. If, however, the disengaged hydrogen is not removed, but be added to the completely or partially decomposed hydride, and the pressure be raised to 45 mm. (at the temperature 330°), the potassium hydride will be re formed. Consequently, both the decomposition and the formation of a body can follow, depending upon whether the external partial pressure be lowered or increased. This pressure is designated the *tension of dissociation*. Similar phenomena occur at higher temperatures, the corresponding pressure, of course, increasing by regular steps. Appended are tensions of dissociation of potassium and sodium hydrides for different temperatures:—

Temperature.	Tension of Dissociation.	
	K_2H	Na_2H
330°	45 mm.	28 mm.
350°	72 "	57 "
370°	122 "	100 "
390°	363 "	284 "
410°	736 "	594 "
430°	1100 "	910 "

The tension of dissociation is independent of the relative quantity of the dissociated body and of the space which the disengaged gas can occupy, whereas in solutions and absorptions (ammonia by charcoal) the pressure at one and the same temperature increases with the quantity of the absorbed gas.

All exothermic compounds behave like potassium and sodium hydrides when they are decomposed into their components; if the pressure be raised above the tension of dissociation the components reunite—the compounds are re-formed. The decomposition of the endothermic compounds (potassium chlorate into chloride and oxygen) is quite different (pp. 29 and 94). It proceeds with heat disengagement ($KCl,O_3 = -$ 11.0 Cal.), corresponding to the chemical affinities, and is only induced by application of external heat. It is independent of external pressure, and there is no reunion of the decomposition products upon increasing the external pressure or upon lowering the temperature. These decompositions are, therefore, quite different from the dissociation of exothermic compounds.

We must also not omit mentioning the great analogy between the phenomena of dissociation and the vaporizing of liquids, which occurs in a similar manner. Like dissociated bodies, liquids exhibit at all temperatures a definite tension in vapor form; the evaporation is conditioned by this. The evaporation will occur in a closed space by the lowering of the pressure, but if the latter be raised the vapors will condense.

Consequently, we observe that the phenomena of dissociation reveal an intimate connection between the forces of chemical affinity and those of physical cohesion.

Potassium forms three oxygen compounds, of which only the following yields corresponding salts.

Potassium Oxide—K_2O—results from the oxidation of thin pieces of metallic potassium in dry air, and by heating potassium peroxide with metallic potassium.

It is a white powder, fusing at a red heat, and evaporating at higher temperatures. It unites with water, with evolution of much heat, and the formation of potassium hydroxide. When heated in a stream of hydrogen it yields the hydroxide, and metallic potassium is separated:—

$$K_2O + H = KOH + K.$$

This peculiar behavior is explained by the heat of formation of KOH (103.9 C.) being greater than that of K_2O (97.1); hence the reaction occurs according to the preceding equation and heat is disengaged. Conversely, KOH cannot, therefore, be decomposed by potassium with the production of K_2O (Beketoff).

Potassium peroxide, KO_2 or K_2O_4, and *potassium suboxide*, K_4O, are very unstable, and readily pass into potassium oxide. The first is formed together with potassium oxide, by the combustion of potassium in dry air or oxygen, and is a yellow mass. The suboxide has a violet color, due to the oxidation of potassium vapors.

Potassium Hydroxide, or *Caustic Potash*—KOH—is obtained by the action of potassium or its oxide upon water. For its preparation, potassium carbonate is decomposed by calcium hydroxide (slaked lime):—

$$K_2CO_3 + Ca(OH)_2 = CaCO_3 + 2KOH.$$

The solution of 1 part potassium carbonate in 10–12 parts water is boiled with 1 part slaked lime in an iron pot, until a filtered portion does not effervesce when hydrochloric acid is added; *i. e.*, until there is no longer any carbonic acid present. On standing awhile, the insoluble calcium carbonate subsides, and the liquid becomes clear. The solution of potassium hydroxide is then poured off, evaporated, the residue melted in a silver dish (which it does not attack), and poured into moulds. The caustic potash, prepared in this way, is not entirely pure, but contains potassium chloride and other salts. To obtain a product that is chemically pure, fuse potassium nitrate with copper filings, and treat the fusion with water.

Potassium hydroxide forms a white, crystalline mass that fuses rather easily, and volatilizes undecomposed at a very high temperature. Exposed to the air it deliquesces, as it absorbs water and carbon dioxide and changes into carbonate. It is very soluble in alcohol, and especially in water. The solution possesses a strong alkaline reaction, saponifies the fats, and has a corrosive action upon the skin and organic tissues; hence it cannot be filtered through paper. At low temperatures the hydrate $KOH+2H_2O$ crystallizes out from concentrated solutions.

The haloid salts of potassium are obtained by the direct union of the halogens with potassium, and by the saturation of the hydroxide or carbonate with haloid acids. They are readily soluble in water, have a salty taste, and crystallize in cubes. When heated they melt, and are somewhat volatile.

Potassium Chloride—KCl—occurs in Stassfurt in large deposits, as *sylvite*, and combined with magnesium chloride exists as *carnallite* ($MgCl_2$, $KCl+6H_2O$). The latter salt serves as the chief source for the preparation of potassium chloride, which meets with varied application in the arts, and also for the preparation of potassium carbonate. The chloride crystallizes in vitreous cubes, of specific gravity 1.84. It melts at 734°, and volatilizes at a strong red heat. 100 parts water dissolve 30 parts of the salt at 0°, and 59 parts at 100°.

Potassium Bromide—KBr—is generally obtained by warming a solution of potassium hydroxide with bromine, when the bromate is also produced:—

$$6KOH + 3Br_2 = 5KBr + KBrO_3 + 3H_2O.$$

The solution is evaporated to dryness, mixed with charcoal, and ignited, which reduces the bromate to bromide:—

$$KBrO_3 + 3C = 3CO + KBr.$$

It is readily soluble in water and alcohol; forms cubes of sp. gr. 2.4, and melts at 699°.

Potassium Iodide—KI—may be prepared like the preceding. It is usually obtained according to the following method: Iodine and iron filings are rubbed together under water, and potassium carbonate added to the solution of the iron iodide; this will precipitate ferrous-ferric oxide; carbon dioxide escapes, and potassium iodide will be found in the solution. It forms large white crystals, fuses at 634°, and is tolerably volatile. Its specific gravity equals 2.9. At medium temperatures it dissolves in 0.7 parts water and 40 parts of alcohol. The aqueous solution dissolves iodine in large quantity. Many metallic insoluble iodides dissolve in it without difficulty, forming double iodides, *e.g.*, $HgI_2.2KI$. The iodide is employed in medicine and photography.

Potassium Fluoride—KFl—is obtained by dissolving the carbonate in aqueous hydrofluoric acid. It crystallizes in cubes at ordinary temperatures, with $2H_2O$, but above 35° does not contain water of crystallization. It is very soluble in water. The aqueous solution attacks glass. It is greatly inclined to combine with other fluorides: KFl.HFl; $BFl_3.KFl$. On adding hydrofluosilicic acid to the solution of potassium salts, a gelatinous precipitate of potassium silicofluoride is thrown down, which dissolves with difficulty in water.

Potassium Cyanide—KCN.—This salt can be produced by saturating potassium hydroxide with hydrocyanic acid, and by heating yellow prussiate of potash (see Iron). It forms a white, easily fusible mass, which deliquesces in the air. The solution may be easily decomposed. It crystallizes in cubes, has an alkaline reaction, and smells like prussic acid, as this is set free by the carbon dioxide of the air. By fusion potassium cyanide reduces many oxides, and hence is employed in reduction processes. It is just as poisonous as prussic acid. It is applied in many ways, especially in photography and for galvanic silvering and gilding.

Potassium Chlorate—$KClO_3$.—The following reaction occurs when chlorine gas is conducted through a hot concentrated potassium hydroxide solution:—

$$6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O.$$

When the solution cools, the difficultly soluble potassium chlorate separates out. It is generally made, in trade, by the action of chlorine upon a mixture of calcium hydroxide and potassium chloride. The reaction occurs in two phases; first, calcium chlorate is formed:—

$$6Ca(OH)_2 + 6Cl_2 = 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O;$$

this then reacts with the potassium chloride:—

$$Ca(ClO_3)_2 + 2KCl = 2KClO_3 + CaCl_2.$$

Potassium chlorate crystallizes from the hot solution in shining tables of the monoclinic system, which dissolve with difficulty in water (100 parts at the ordinary temperature dissolve 6 parts of the salt). Its taste is cooling and astringent. When heated it melts (at 359°) giving up a portion of its oxygen, and changes to the **Perchlorate**—$KClO_4$—which on further heating decomposes into oxygen and potassium chloride (see p. 182). As it gives up oxygen readily, it serves as a strong oxidizing agent. With hydrochloric acid it liberates chlorine :—

$$KClO_3 + 6HCl = KCl + 3H_2O + 3Cl_2.$$

Mixed with sulphur, or certain sulphides, it explodes on heating and when struck a sharp blow. The igniting material upon the so-called Swedish (parlor) matches consists of antimony sulphide and potassium chlorate; when this is rubbed upon the friction surface coated with red phosphorus it ignites.

Potassium Hypochlorite—$KClO$—is formed when chlorine is permitted to act upon a cold solution of potassium hydroxide :—

$$2KOH + Cl_2 = KCl + KClO + H_2O.$$

It only exists in aqueous solution; when the latter is evaporated the salt is decomposed into chloride and chlorate :—

$$3ClOK = 2KCl + ClO_3K.$$

The solution has an odor resembling that of chlorine, and bleaches strongly, especially upon the addition of acids. The bleaching solutions occurring in trade (Eau de Javelle) are prepared by the action of chlorine upon solutions of sodium and potassium carbonates; they also contain free hypochlorous acid.

The oxy-salts of bromine and iodine are perfectly analogous to those of chlorine. *Potassium Bromate*—$KBrO_3$—and *Potassium Iodate*—KIO_3—are prepared by the action of bromine or iodine upon hot potassium hydroxide; the second is also produced by the action of iodine upon potassium chlorate, when the chlorine is directly replaced (p. 186). If chlorine be passed through a hot solution of potassium iodate in potassium hydroxide—the periodate of potassium, KIO_4, arises; it is difficultly soluble and when heated decomposes into O and KIO_3, which then breaks up into potassium iodide and oxygen.

Besides the normal periodates, KIO_4, $NaIO_4$, other salts exist which are derived from the highest hydroxyl compound, $I(OH)_7$, and its anhydro-derivatives (p. 185). These salts are very numerous, and are in part monoperiodates, $IO(OH)_5$ and $IO_2(OH)_3$, and partly polyperiodates, produced by the condensation of several molecules of the highest hydroxides, *e.g.*, $I_2O_3(OH)_8$ and $I_2O_5(OH)_4$.

Potassium Sulphate—K_2SO_4—is formed in the action of sulphuric acid upon potassium chloride, and as a by-product in many technical operations. It crystallizes without water, in small rhombic prisms, having a bitter, salty taste, and dissolves in 10 parts H_2O of ordinary temperature. It is employed principally for the preparation of potassium carbonate, according to the method of Le Blanc. (See Soda.)

The *acid* or *primary* salt—$HKSO_4$—crystallizes in large rhombic tables, and is very readily soluble in water. It fuses about 200°, loses water, and is converted into potassium pyrosulphate—$K_2S_2O_7$ (p. 198)—which at 600° yields K_2SO_4 and SO_3.

The salts of sulphurous acid—the *primary*, SO_3KH, and the *secondary sulphites*, SO_3K_2—are produced when SO_2 comes in contact with a potassium carbonate solution; they are very soluble and crystallize with difficulty. The first salt shows an acid, the second an alkaline reaction. If sulphur dioxide be passed into a solution of potassium carbonate until effervescence ceases and then cooled, the pyrosulphite—$K_2S_2O_5$—corresponding to the pyrosulphate, will crystallize out.

Potassium Nitrate, Saltpetre, KNO_3, does not occur anywhere in large quantities, but is widely distributed in the upper strata of the earth and is found as an efflorescence on the soil in some regions of the hot zone (in Egypt and East India). It is produced whenever nitrogenous organic substances decay in the presence of potassium carbonate—conditions which are present in almost every soil. The intentional introduction of these is the basis of the artificial nitre production in the so-called saltpetre plantations. Manures and various animal offals are mixed with wood ashes (potassium carbonate) and lime, arranged in porous layers, and submitted to the action of the air for two or three years, when nitrates are produced from the slow oxidation of the nitrogen. The heaps are then treated with water and potassium carbonate added to the solution, which contains potassium, calcium and magnesium nitrates, to convert the last two salts into potassium nitrate:—

$$Ca(NO_3)_2 + K_2CO_3 = CaCO_3 + 2KNO_3.$$

The precipitate of calcium and magnesium carbonate is filtered off and the solution evaporated. The procedure was formerly employed universally in the manufacture of potassium nitrate. At present, however, almost all of it is obtained by the decomposition of the sodium salt, occurring in large deposits in Chili, by means of potassium carbonate or chloride:—

$$NaNO_3 + KCl = NaCl + KNO_3.$$

Warm saturated solutions of sodium nitrate and potassium chloride are mixed and boiled, when sodium chloride, being less soluble in hot water, will separate. On cooling the solution potassium nitrate, being less soluble in cold water, crystallizes out; sodium chloride is about equally soluble in hot and cold water, for which reason the portion not separated by boiling remains in solution.

Potassium saltpetre crystallizes without water of crystallization in large six-sided rhombic prisms. It is far more soluble in hot than in cold water; 100 parts of water dissolve 244 parts at 100°, but at 0° only 13 parts. It possesses a cooling taste, fuses at 338°, and decomposes, when further heated, into oxygen and potassium nitrite, KNO_2. Heated with carbon it yields potassium carbonate:—

$$4KNO_3 + 5C = 2K_2CO_3 + 3CO_2 + 2N_2.$$

Its principal use is in the manufacture of gunpowder. This is a granular mixture of potassium nitrate, sulphur, and charcoal. The relative quantities of these constituents are somewhat different in the various kinds of powder (sporting, blasting, and cannon). Upon an average, the powder consists of 75 per cent. KNO_3, 12 per cent. sulphur, and 13 per cent. carbon, which closely corresponds to the atomic composition $2KNO_3 + S + 3C$. When the powder burns, its decomposition is approximately expressed by the following equation:—

$$2KNO_3 + S + 3C = K_2S + 3CO_2 + N_2.$$

The effectiveness of the powder, therefore, depends upon the disengagement of carbon dioxide and nitrogen gas, the volume of which is almost 1000 times as great as that of the decomposed powder.

Potassium Nitrite—KNO_2—is obtained by fusing saltpetre with lead, which withdraws one atom of oxygen from the former. A white, fusible mass results; this deliquesces in the air.

The potassium salts of *phosphoric acid:* K_3PO_4, K_2HPO_4, and KH_2PO_4, meet with no practical application, they are readily soluble in water and crystallize poorly; therefore, the sodium salts are generally used. The borates, BO_2K and $B_4O_7K_2 + 5H_2O$ (see Borax), crystallize with difficulty.

Potassium Carbonate—K_2CO_3—ordinarily known as **potashes**, is a principal ingredient of plant ashes. The field plants absorb potassium salts from the earth; these are then transformed in them into salts of organic acids. When the plants are burned the organic acids are destroyed and potassium carbonate remains. The ashes are lixiviated with hot water, the filtrate evaporated and the residue ignited. The *crude potashes* thus obtained contain, besides the carbonate, also chloride, sulphate, and other salts. To purify them, treat with a little water, which will dissolve the easily soluble carbonate, leaving nearly all of the other ingredients behind. In this way we obtain pure potashes. This method of getting potashes from plant ashes was formerly pursued extensively in America, Hungary, and Russia; it is not much used at present, because potassium carbonate is, upon the one hand, replaced by the cheaper sodium carbonate in practice; on the other hand, the immense deposits in Stassfurt and Galicia afford an inexhaustible supply of potassium salts. Considerable quantities of potassium carbonate, used at present almost entirely for the production of Bohemian or crystal glass, have been recently obtained from Stassfurt, according to the methods employed in the preparation of sodium carbonate from the chloride. (See Soda.) Chemically pure potassium carbonate is obtained most conveniently by the ignition of cream of tartar or by heating the primary carbonate.

The commercial carbonate is a white, deliquescent powder melting at 830°, and vaporizing at a red heat. It crystallizes from concentrated aqueous solutions with 1½ molecules of water, in monoclinic prisms; at 100° it loses ½ molecule water. The solution has a caustic taste and shows an alkaline reaction. When CO_2 is conducted through the liquid it is absorbed and *primary potassium carbonate* is produced :—

$$CO_3K_2 + H_2O + CO_2 = 2KHCO_3.$$

This salt, ordinarily called *bi-carbonate*, crystallizes in monoclinic prisms, free from water. It dissolves in 3–4 parts water and exhibits a neutral reaction. Heated to 80°, it decomposes into K_2CO_3,CO_2 and water. The decomposition of the dry salt does not begin until about 110°, while the aqueous solution decomposes even on evaporation.

Potassium Silicate, water-glass, does not possess a constant composition and cannot be obtained crystallized. It is produced by solution of silicic acid or amorphous silicon dioxide in potassium hydroxide, or by the fusion of silica with potassium hydroxide or carbonate. The concentrated solution dries, when exposed, to a glassy, afterward opaque mass, which, when reduced to a powder, will dissolve in boiling water. Potassium (and also sodium) water-glass has an extended application, especially in cotton printing, for the fixing of colors (stereochromy), in rendering combustible material fireproof, in soap boiling, etc.

SULPHUR COMPOUNDS OF POTASSIUM.

Potassium Hydrosulphide—KSH—is obtained when potassium hydroxide is saturated with hydrogen sulphide :—

$$KOH + H_2S = KSH + H_2O.$$

Evaporated *in vacuo* it crystallizes in colorless rhombohedra, of the formula $2KSH + H_2O$, which deliquesce in the air. At 200°, it loses its water of crystallization, and at a higher temperature fuses to a yellowish liquid, which solidifies to a reddish mass. Like the hydroxide, it has an alkaline reaction. On adding an equivalent quantity of potassium hydroxide to the sulphydrate solution, we get potassium sulphide:—

$$KSH + KOH = K_2S + H_2O.$$

Potassium Sulphide—K_2S—is usually obtained by fusing potassium sulphate with carbon:—

$$K_2SO_4 + 2C = K_2S + 2CO_2.$$

When fused, it solidifies to a red crystalline mass. It crystallizes from concentrated aqueous solutions with 5 molecules of H_2O, in colorless prisms, which deliquesce in the air. The solution absorbs oxygen from the latter, and is decomposed into potassium hyposulphite and caustic potash:—

$$2K_2S + H_2O + 2O_2 = K_2S_2O_3 + 2KOH.$$

Potassium hydrosulphide and sulphide precipitate insoluble sulphides from the solutions of many metallic salts. They are decomposed by acids with liberation of hydrogen sulphide.

When the aqueous solution of the sulphide is boiled with sulphur the *polysulphides*, K_2S_3, K_2S_4, and K_2S_5, are formed, which after fusion solidify to yellowish-brown masses. The aqueous solutions of the polysulphides are decomposed by acids, with disengagement of H_2S and separation of sulphur (milk of sulphur). The so-called *liver of sulphur* (*Hepar sulphuris*), a liver-brown mass, used in medicine, is obtained by the fusion of potassium carbonate with sulphur, and consists of a mixture of potassium polysulphides with potassium sulphate.

The aqueous solution of the potassium, as well as that of the sodium sulphide, dissolves some metallic sulphides and forms sulpho-salts with them (p. 226).

When dry ammonia is conducted over heated potassium, potassamide (NH_2K) results. This is a dark-blue liquid which solidifies to a yellowish-brown mass. Water decomposes it into potassium hydroxide and ammonia. When potassamide is ignited away from the air, it loses ammonia, and leaves behind potassium triamide, NK_3, a blackish compound which is spontaneously inflammable.

Recognition of the Potassium Compounds.—Almost all the potassium compounds are easily soluble in water, with the exception of a few, which, therefore, serve for the characterization and separation of potassium. Tartaric acid added to the solution of a potassium salt gives a crystalline precipitate of acid potassium tartrate. Platinic chloride ($PtCl_4$) produces in potassium solutions a yellow, crystalline precipitate of $PtCl_4.2KCl$. Potassium compounds introduced into the flame of an alcohol or gas lamp impart to the same a *violet* coloration. The spectrum of the flame is characterized by two bright lines, one red and one violet (see Spectrum Analysis).

RUBIDIUM AND CÆSIUM.

Rb = 85.2. Cs = 132.7.

Rubidium and Cæsium are the perfect analogues of potassium (p. 278). They were discovered by means of the spectroscope, by Bunsen and Kirchhoff, in 1860. Although only occurring in small quantities, they are yet very widely distributed, and frequently accompany potassium in mineral springs, salt, and plant ashes. The mineral lepidolite contains 0.5 per cent. of rubidium; upward of 30 per cent. of cæsium oxide is present in the very rare pollucite, a silicate of aluminium and cæsium. The spectrum of rubidium is marked by two red and two violet lines; cæsium by two distinct blue lines; hence, the names of these elements.

Rubidium and cæsium form double chlorides ($PtCl_4$. 2RbCl) with platinum chloride, and they are more insoluble than the double platinum salt of potassium, hence may answer for the separation of these elements from potassium. Rubidium and cæsium may be obtained free by decomposing their fused chlorides with the electric current. Rubidium is also prepared by igniting its carbonate with charcoal. Metallic rubidium has a silver-white color, with a somewhat yellowish tinge; its vapor is greenish-blue. Metallic cæsium has been obtained by the electrolysis of a mixture of cæsium and barium cyanides. Electrodes of aluminium are employed for this purpose. Cæsium is a silver white metal, of sp. gr. 1.85. It oxidizes quite readily and inflames in the air. It melts at 26.5° and boils at 270°.

SODIUM.

Na = 23.06.

Sodium is widely distributed in nature, especially as chloride in sea water and as rock-salt; and is also found in silicates. The metal was obtained in 1807, by Davy, by the action of a strong electric current upon fused sodium hydroxide. At present, like potassium, it is obtained upon a large scale by igniting a mixture of sodium carbonate and carbon in an iron retort:—

$$Na_2CO_3 + 2C = 2Na + 3CO.$$

The liberated sodium vapors are condensed on flat iron receivers of peculiar construction, and the liquefied sodium collected under rock-oil.

Sodium in external properties is very similar to potassium. It melts at 95.6°, distils at a red heat, and is converted into a colorless vapor, which burns with a bright yellow flame in the air. It oxidizes readily on exposure, and decomposes water even in the cold, although less energetically than potassium. A piece of sodium thrown upon water swims about upon the surface with a rotatory movement, the disengaged hydrogen, however, not igniting. If we prevent the motion, by confining the metal to one place, the heat liberated by the reaction attains the ignition temperature of hydrogen, and a flame follows.

Sodium Oxide,—Na_2O, and **suboxide,** Na_4O, are very similar to tne corresponding potassium compounds; the peroxide, is somewhat different. It is obtained by burning sodium in a stream of oxygen. Its formula is Na_2O_2. When heated it absorbs iodine vapors, forming the compound, Na_2OI_2 ($Na_2O_2 + I_2 = Na_2OI_2 + O$), soluble in water, but decomposed by acids into free iodine and sodium salt. This compound like some others, seems to indicate that sodium has several valences.

When heated with hydrogen sodium oxide is decomposed with separation of metallic sodium and formation of sodium hydroxide. This is explained by the fact that the heat of formation of NaOH is greater than that of Na_2O (p. 279). Carbon monoxide decomposes sodium monoxide in a similar manner, when the latter is heated to 290–310°:—

$$2Na_2O + CO = Na_2CO_3 + Na_2.$$

This reaction occurs because the heat of formation of sodium carbonate (271.2 C.) is greater than that of $2Na_2O$(2 . 100.2 C.) and CO(30.1 C.). Na_2O combines with CO_2 about 400° with production of light and yields CO_3Na_2(Na_2O, CO_2 = 74.1 C.).

Sodium Hydroxide, Sodium Hydrate, or Caustic Soda, NaOH, like potassium hydroxide, is formed by boiling a solution of sodium carbonate with calcium hydroxide:—

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2NaOH.$$

At present it is directly produced in the soda manufacture by adding a little more carbon to the fusion (see Soda), or by igniting sodium carbonate (Löwig) with ferric oxide, which affords a compound of $Fe_2O_3.Na_2O$, decomposed by warm water into ferric oxide and sodium hydroxide.

The sodium hydroxide which solidifies after fusion is a white, radiating, crystalline mass, and resembles caustic potash very much. It attracts water from the air, becomes moist, and coats itself by carbon dioxide absorption with a white layer of sodium carbonate (caustic potash deliquesces perfectly, because the resulting carbonate is also deliquescent). The aqueous solution, called sodium hydroxide, resembles that of potassium. Crystals of $NaOH + 3\frac{1}{2}H_2O$ separate at 0° from the concentrated solution; they melt at 6°.

Sodium Chloride—NaCl—is abundant in nature. It is found almost everywhere in the earth and in natural waters; in sea-water it averages 2.7–3.2 per cent. As rock-salt it forms large deposits in many districts—at Stassfurt and Wielizca in Galicia.

In warm climates, on the coasts of the Mediterranean Sea, sodium chloride is gotten from the sea, according to the following procedure. At high tide, sea-water is allowed to flow into wide, flat basins (salt gardens), in which it evaporates under the sun's heat; the working is limited, therefore, to summer time. After sufficient concentration, pure sodium chloride first separates, and this is collected by itself. Later, there crystallizes a mixture of sodium chloride and magnesium sulphate; finally potassium chloride, magnesium chloride and some other salts appear (among them potassium iodide and bromide), the separation of which constitutes a particular industrial branch in some regions. In cold climates, as in Norway and at the White Sea, the cold of winter is employed for the production of salt. In the freezing of sea-water, as well as of other solutions, almost pure ice separates at first; the enriched sodium chloride solution is then concentrated in the usual way.

The *rock-salt* is either mined in shafts, or, where the strata are not so large and are admixed with other varieties of rock, a lixiviation process is employed. Borings are made in the earth and water run into them, or into any openings already formed. When the water has saturated itself with sodium chloride, it is pumped to the surface and the brine then further worked up. In many regions, especially in Reichenhall, in Bavaria, more or less saturated natural salt or brine springs flow from the earth. The concentration of the non-saturated brine occurs at first in the so-called "graduation" houses. These are long wooden frames filled with fagots, and on letting the salt water run upon them it will be distributed and evaporated by the fall; the concentrated brine collects in the basin below, and is then evaporated over a free fire.

Sodium chloride crystallizes from water in transparent cubes, which arrange themselves by slow cooling into hollow, four-sided pyramids. It melts at 772° and volatilizes at a white heat. It is slightly more soluble in hot than in cold water; 100 parts at 0° dissolve 36 parts salt; at 100°, 39 parts. The saturated solution, therefore, contains 26 per cent. sodium chloride. The specific gravity of the crystals equals 2.13. If the saturated solution be cooled below —10°, large monoclinic tables ($NaCl + 2H_2O$) separate; these lose water at 0° and become cubes.

The ordinary sodium chloride usually contains a slight admixture of magnesium salts, in consequence of which it gradually deliquesces in the air; the perfectly pure salt is not hygroscopic. When heated the crystals crackle, because of the escape of the mechanically enclosed water.

Sodium Bromide and iodide crystallize at ordinary temperatures with 2 molecules of H_2O, which they lose again at 30°; above 30° they separate in anhydrous cubes. Sodium bromide fuses at 708° and the iodide at 628°; the former is difficultly soluble in alcohol and the latter is very soluble.

Sodium Chlorate ($NaClO_3$) and **perchlorate** ($NaClO_4$) are considerably more soluble in water than the corresponding potassium salts.

Sodium Iodate—$NaIO_3$—is obtained the same as the potassium salt, and crystallizes at ordinary temperatures with 3 molecules of H_2O in silky needles. If chlorine gas be conducted through the warmed solution of sodium iodate in sodium hydroxide, the periodate $IO\left\{\begin{matrix}(ONa)_2\\(OH)_3\end{matrix}\right.$ (see p. 184) crystallizes out on cooling. This becomes the normal salt ($NaIO_4 + 3H_2O$) when dissolved in nitric acid.

Sodium Sulphate—Na_2SO_4—crystallizes at ordinary temperatures with 10 molecules of water of crystallization, and is then known as Glauber's salt (*Sal mirabile Glauberi*). It occurs in many mineral waters, and in large deposits, with or without water of crystallization, in Spain. It is a by-product in the manufacture of sodium chloride from sea-water and brine. It is produced in large quantities by heating salt with sulphuric acid:—

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl,$$

and is used in making soda (sodium carbonate). Or it may be prepared by the method of Hargreaves, by conducting SO_2, air and steam over strongly ignited sodium chloride:—

$$2NaCl + SO_2 + O + H_2O = SO_4Na_2 + 2HCl.$$

More recently the sulphate has been obtained by a transposition of sodium chloride with magnesium sulphate at a winter temperature —a procedure which is prosecuted chiefly in Stassfurt, where immense quantities of magnesium sulphate exist:—

$$2NaCl + SO_4Mg = MgCl_2 + SO_4Na_2.$$

Sodium sulphate crystallizes at ordinary temperatures with 10 molecules of H_2O, in large, colorless, monoclinic prisms, which crumble in the air and fall into a white powder. When the salt is heated to 33°, it fuses in its own water of crystallization; by further increase of temperature it gradually loses this, becomes solid, and again fuses at a red heat. The solubility of Glauber's salt ($Na_2SO_4 + 10 H_2O$) shows the following interesting deportment: 100 parts of water dissolve, at 0°, 12 parts; at 18°, 48 parts; at 25°, 100 parts; at 30°, 200 parts; at 33°, 327 parts of the hydrous salt. At the last temperature the solubility is greatest; by further increase of heat it gradually diminishes; at 50°, 100 parts water dissolve only 263 parts; at 100°, 238 parts of the salt. While, ordinarily, the solubility increases with temperature, Glauber's salt exhibits a varying deportment. This is explained in that the hydrate, $Na_2SO_4 + 10H_2O$, in aqueous solution, above the temperature of 33°, decomposes into water and the salt, $Na_2SO_4 + H_2O$, which is less soluble in water. The decomposition does not occur at once, but only gradually, with increasing temperature, for which reason the quantity of the salt dissolved gradually grows less. Here we have an example of dissociation taking place in aqueous solution (p. 196). The solution, saturated at 33°, becomes turbid upon heating, and a portion of the dissolved salt separates in anhydrous, small, rhombic octahedra.

The following interesting deportment in the solution of Glauber's salt may also be noticed. When the solution, saturated at 33°, is allowed to cool to the ordinary temperature, and even lower, not the slightest separation of crystals occurs, although the salt is vastly more insoluble at lower temperatures than at 33°. Many other salts form *supersaturated solutions*, although they are less striking than that of Glauber's salt. The supersaturated solution of the latter may be agitated and twirled about without crystallization setting in. If, however, a glass rod, or some other solid body, be introduced into the solution, it will solidify suddenly to a crystalline mass. The particles of dust floating about in the air will have a like effect: therefore, to preserve the supersaturated solution, the vessel containing it should be kept well corked. By accurately made investigations, it has been determined that the crystallization of the supersaturated Glauber's salt solution is only induced by contact with already formed crystals. These must then be present everywhere in the atmosphere, because only solids which have been exposed to the air, and have not been carefully cleansed afterward, bring about the crystallization. Hence, the formation of a crystal of Glauber's salt is always dependent upon the previous existence of a similar crystal—just as the production of cells is only caused by cells.

In the crystallization of a supersaturated Glauber's salt solution, considerable heat is disengaged, and the mass increases in temperature. This is because the latent heat of all substances in the liquid condition is greater than in the solid. At 10°, occasionally, and of their own accord, transparent crystals, $Na_2SO_4 + 7H_2O$, separate from the supersaturated solutions. Exposed to the air and in contact with solid bodies, these crystals are changed to anhydrous sodium sulphate and Glauber's salt.

This salt is employed in medicine as a purgative, and finds extended application in the manufacture of glass and the preparation of soda.

The **primary** or **acid sodium sulphate**—$NaHSO_4$—is obtained by the action of sulphuric acid upon the neutral salt or upon sodium chloride:—

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

At ordinary temperatures, it crystallizes with one molecule of water, and is perfectly analogous to the potassium salt.

The sodium salts of sulphurous acid are obtained by conducting sulphur dioxide into solutions of sodium hydroxide or carbonate. The secondary *sulphite*, Na_2SO_3, crystallizes with 7 molecules of H_2O at ordinary temperatures; in the presence of sodium hydroxide, or by warming the solution, it separates in the anhydrous state. The primary *sulphite*—$NaHSO_3$—gives up sulphur dioxide in the air, and is oxidized to sodium sulphate.

Sodium Hyposulphite—$Na_2S_2O_3$—is prepared by boiling the aqueous solution of neutral sodium sulphite with flowers of sulphur:—

$$Na_2SO_3 + S = Na_2S_2O_3.$$

It is obtained as a by-product in the recovery of sulphur from the soda residues.

It crystallizes with five molecules of H_2O, in large monoclinic prisms, dissolves very readily in water, and is somewhat deliquescent in the air. At 56°, it melts in its water of crystallization; loses all water at 100°, and decomposes by further heating into

Na_2SO_4 and Na_2S_5. When the dry salt is heated in the air, the polysulphide burns with a blue flame. Acids decompose the aqueous solution with separation of sulphur and evolution of sulphur dioxide:—

$$S_2O_3Na_2 + 2HCl = 2NaCl + SO_2 + S + H_2O.$$

Like the sulphate, it readily affords supersaturated solutions. The hyposulphite is used as a reducing agent; chlorine, bromine and iodine are converted by it into the corresponding halogen salts:—

$$2S_2O_3Na_2 + I_2 = \underset{\text{Sodium tetrathionate.}}{S_4O_6Na_2} + 2NaI.$$

An iodine solution is instantaneously decolorized by sodium hyposulphite. Chlorine behaves differently; sulphuric acid and sodium chloride are produced. Upon this reaction rests the application of sodium hyposulphite as an antichlor in chlorine bleaching, to remove the excess of the chlorine, which has a destructive action upon the fibre. In consequence of its property of dissolving the halogen silver derivatives, it is employed in photography.

Sodium Carbonate (Soda)—Na_2CO_3.—This, technically, very important salt occurs frequently in nature. In some districts, as in Hungary and in Africa, it disintegrates from the soil, and occurs also in the so-called sodium seas (in Egypt, and upon the coast of the Caspian Sea). It is contained in the ashes of many sea-plants, chiefly the algæ, etc. These assimilate the sodium salts of the earth, while the land-plants absorb the potassium salts, and for this reason contain potashes in their ash. The ash of the sea-plants, called *varec* in Normandy, *kelp* in England, formerly served as the principal material for the preparation of soda. At present it is, however, almost exclusively made in large quantities from sodium chloride, according to a method devised in 1787 by Leblanc.

According to this method, the sodium chloride is converted, by warming with sulphuric acid, into sodium sulphate (p. 292). When the latter is dry, it is mixed with charcoal and chalk, and ignited in a reverberatory furnace. Two principal phases may be distinguished in this reaction. First, the carbon reduces the sodium sulphate:—

$$Na_2SO_4 + 2C = Na_2S + 2CO_2.$$

The sodium sulphide then acts upon the calcium carbonate to form calcium sulphide and sodium carbonate:—

$$Na_2S + CaCO_3 = CaS + Na_2CO_3.$$

At the same time, the high temperature converts a portion of the calcium carbonate into calcium oxide and carbon dioxide, which is reduced by the ignited carbon to the monoxide; the appearance of the latter, which burns with a bluish flame, indicates the end of the action. The chief products in the soda fusion are, then, sodium carbonate, calcium sulphide and oxide; in addition, different other sulphur salts are formed in smaller quantity. The fusion is lixiviated with cold water; the sodium carbonate dissolves, and there remains behind an insoluble compound of calcium sulphide with oxide, $CaO.2CaS$, the *soda residue*. By the evaporation of the solution and the ignition of the residue, we get the commercial or *crude calcined soda*, containing different admixtures, among them sodium hydroxide. The latter is formed by the action of excess of carbon upon sodium carbonate:—

$$Na_2CO_3 + C = Na_2O + 2CO.$$

By purposely adding more carbon to the fusion, sodium hydroxide may be obtained, together with the carbonate. To purify the crude soda it is recrystallized from water; large, transparent crystals, $Na_2CO_3 + 10H_2O$, *crystallized soda*, separate out; the sodium hydroxide remains dissolved.

Considerable quantities of soda are obtained at present from cryolite, a compound of aluminium fluoride and sodium fluoride ($AlFl_3.3NaFl$), which occurs in great deposits in Iceland. The pulverized mineral is ignited with burned lime; insoluble calcium fluoride and a very soluble compound of aluminium oxide with sodium oxide, called sodium aluminate (see Aluminium) are produced:—

$$2(AlFl_3.3NaFl) + 6CaO = 6CaFl_2 + Al_2O_3.3Na_2O.$$

The mass is treated with water and carbon dioxide conducted into the solution, which causes the precipitation of aluminium oxide, and sodium carbonate dissolves:—

$$Al_2O_3.3Na_2O + 3H_2O + 3CO_2 = Al_2(OH)_6 + 3Na_2CO_3.$$

Latterly, a third procedure has appeared. It depends upon the double decomposition of a solution of sodium chloride with primary ammonium carbonate, by heat, under high pressure:—

$$NaCl + CO_3(NH_4)H = NaHCO_3 + NH_4Cl.$$

The primary sodium carbonate being rather insoluble in water, separates from solution, and is converted by heat into the secondary carbonate. The ammonium chloride remains dissolved, and afterward is converted again into carbonate by aid of calcium carbonate. In this way, one and the same quantity of ammonium carbonate will suffice for the conversion of an indefinite quantity of sodium chloride into soda. The technical difficulties which at first opposed the extension of this process, so simple in chemical respects, are now entirely removed, and at present half of all the soda manufactured in Europe is made by this so-called *ammonia process* (Solvay-soda). The reason that the Leblanc method has not been entirely supplanted, is that until now there was no means by which the chlorine of the sodium chloride could be converted into some available form.

At ordinary temperatures sodium carbonate crystallizes with 10 molecules of $H_2O(Na_2CO_3 + 10H_2O)$ in large monoclinic crystals, which crumble upon exposure and become a white powder. It melts at 50° in its water of crystallization, and upon additional application of heat a pulverulent hydrate—$Na_2CO_3 + 2H_2O$—separates, which in dry air has 1 molecule of H_2O, and at 100° loses all of this. At 30°–50° rhombic prisms of the composition $CO_3Na_2 + 7H_2O$, crystallize from the aqueous solution. The anhydrous salt absorbs water from the air but does not deliquesce. It melts at a red heat and volatilizes somewhat at a very high temperature. 100 parts H_2O dissolve 15 parts at 0°, and at 38°, 138 parts of the dry salt. At more elevated temperatures the solubility is less, owing, as in the case of the sulphate, to the formation of less soluble, lower hydrates. Sodium carbonate has a strong alkaline reaction; acids liberate carbon dioxide from it.

Primary Sodium Carbonate—ordinary Bicarbonate of Soda—*Natrium Bicarbonicum*—$NaHCO_3$—is produced by the action of carbon dioxide upon the hydrous secondary carbonate:—

$$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3.$$

It crystallizes without water, in small monoclinic tables; it dissolves, however, at ordinary temperatures in 10–11 parts water, and possesses feeble alkaline reaction. By heating and boiling the solution it passes into the secondary carbonate with disengagement of carbon dioxide. The salt decomposes rapidly even under 100°. By rapid evaporation small monoclinic prisms of the so-called sodium sesquicarbonate—$C_3O_8Na_4 + 3H_2O$ or $Na_4H_2(CO_3)_3 + 2H_2O$, separate; this also deposits in the sodium seas of Hungary and Egypt. It is called *Trona* or *Urao*.

Sodium Nitrate—$NaNO_3$—Chili saltpetre, is found in immense deposits in Peru. It crystallizes in rhombohedra very similar to cubes, hence designated *cubic saltpetre*. It fuses about 318°. In water it is somewhat more easily soluble than potassium saltpetre. In the air it attracts moisture, hence it is not adapted to the manufacture of gunpowder. In other respects it is perfectly similar to potassium nitrate. It is largely used in the manufacture of nitric acid, and especially in preparing potassium saltpetre (p. 285).

Sodium Nitrite, $NaNO_2$, is prepared like potassium nitrite (p. 286), by heating sodium nitrate with lead, iron, or graphite. It crystallizes more readily than potassium nitrite, and does not deliquesce in the air. It occurs in trade in small colorless crystals, containing from 93–98 per cent. of the pure salt. It is largely used in the dye industry for the preparation of the azo-compounds.

Sodium Phosphates. The sodium salts of phosphoric acid are less soluble and crystallize better than those of potassium. The *tri-sodium phosphate*—Na_3PO_4—is made by saturating 1 molecule of phosphoric acid with 3 molecules of NaOH, and crystallizes in six-sided prisms with 12 molecules of H_2O. It has a strong alkaline reaction, absorbs carbon dioxide from the air, and is converted into the secondary salt.

Di-sodium Phosphate—Na_2HPO_4—is the most stable of the sodium phosphates, and hence, is generally employed in laboratories (*Natrium phosphoricum*). It may be obtained by saturating phosphoric acid with sodium hydroxide to feeble alkaline reaction, or may be prepared on a large scale by decomposing bone ashes (tricalcium phosphate) with an equivalent amount of sulphuric acid. It crystallizes at ordinary temperatures with $12H_2O$ in large monoclinic prisms which effloresce rapidly upon exposure. It separates from solutions with a temperature above 30° in non-efflorescing crystals containing 7 mols. H_2O. It is soluble in 4–5 parts water, and shows a feeble alkaline reaction. The solution absorbs large quantities of carbon dioxide, without suffering any alteration. When heated the salt loses water, melts about 300° and becomes *Sodium Pyrophosphate*—$Na_4P_2O_7$—which crystallizes with 10 molecules of H_2O, and upon boiling with nitric acid passes into primary sodium phosphate.

The *primary* or *monosodium phosphate*—NaH_2PO_4, crystallizes with 1 molecule of H_2O, and exhibits an acid reaction. At 100° it loses its water of crystallization, and at 200° becomes $Na_2H_2P_2O_7$, *disodium pyrophosphate*, which at 240° forms *sodium metaphosphate* —$NaPO_3$:—

$$H_2Na_2P_2O_7 = 2NaPO_3 + H_2O.$$

We get various modifications of the metaphosphate, according to the conditions of fusing and cooling; they are probably polymerides, corresponding to the formulas $Na_2P_2O_6$, $Na_3P_3O_9$, etc. Upon heating sodium metaphosphate with metallic oxides the latter dissolve, and salts of orthophosphoric acid are formed, *e. g.*:—

$$NaPO_3 + CaO = NaCaPO_4.$$

In this manner, characteristic colored glasses (phosphorus beads) are obtained with various metals. In blowpipe analysis this behavior serves for the detection of the respective metals.

The salts of arsenic acid are perfectly analogous to those of phosphoric acid. Of the antimoniates may be mentioned the disodium pyroantimoniate, $Na_2H_2Sb_2O_7 + 6H_2O$, which is insoluble in cold water, and is therefore precipitated from the soluble sodium salts on the addition of dipotassium pyroantimoniate.

Sodium Borate. The normal salts of boric acid, $B(OH)_3$, and metaboric acid, $BO.OH$ (see p. 245), are not very stable. The ordinary alkaline borates are derived from tetraboric acid ($H_2B_4O_7$), which results from the condensation of 4 molecules of the normal boric acid:—

$$4B(OH)_3 - 5H_2O = H_2B_4O_7.$$

The most important of the salts is *borax*, which crystallizes at ordinary temperatures with 10 molecules of H_2O in large monoclinic prisms, $Na_2B_4O_7 + 10H_2O$. Borax occurs naturally in some lakes of Thibet, whence it was formerly imported under the name of *tinkal*. At present, it is prepared artificially by boiling or fusing boric acid with sodium carbonate. At ordinary temperatures, the crystals dissolve in 14 parts water; at 100° in one-half part; and the solution has a feeble alkaline reaction. When heated to 70° rhombohedra crystallize from the solution, and have the composition $Na_2B_4O_7 + 5H_2O$, formerly known as *octahedral borax*. Both salts puff up when heated, lose water, and yield a white, porous mass (*burned borax*), which fuses at 561° to a transparent vitreous mass ($Na_2B_4O_7$). In fusion this dissolves many metallic oxides, forming transparent glasses (*borax beads*), which frequently possess characteristic colors; thus copper salts give a blue, chromic oxide, a green glass. Therefore, borax may be employed in blowpipe tests for the detection of certain metals. Upon this property of dissolving metallic oxides depends the application of borax for the fusion and soldering of metals.

Sodium Silicate—sodium water glass—is analogous to the potassium salt, and is most readily obtained by fusing quartz with sodium sulphate and charcoal.

The sulphur compounds of sodium are also analogous to those of potassium.

Recognition of Sodium Compounds.—Almost all the sodium salts are easily soluble in water, sodium pyroantimoniate—$H_2Na_2Sb_2O_7$—excepted; this is precipitated from solutions of sodium salts by potassium pyroantimoniate, and can serve for the detection of sodium. Sodium compounds, exposed in a colorless flame, impart to the latter an intense yellow. The spectrum of the sodium flame is characterized by a very bright yellow line, which, when more strongly magnified, splits into two lines.

LITHIUM.

$Li = 7.03$.

Lithium only occurs in nature in small quantities, but is tolerably widely disseminated, and is found in some mineral springs and in the ashes of many plants, notably in that of tobacco and the beet. As a compound silicate, it occurs in lepidolite or lithia mica; as phosphate (with iron and manganese) in triphylite.

The metal is separated from the chloride by means of the electric current, and is silver-white in color, decomposing water at ordinary temperatures. Its specific gravity is 0.59. It is the lightest of all the metals, and swims upon naphtha. It melts at 180°, and burns with an intense white light.

The lithium salts are very similar to the salts of sodium, but closely approach those of magnesium (p. 278).

Lithium Chloride—LiCl—crystallizes, at ordinary temperatures, in anhydrous, regular octahedra; below 10°, however, it has two molecules of H_2O, and deliquesces in the air.

Lithium Phosphate—$Li_3PO_4 + \frac{1}{2}H_2O$—and **Lithium Carbonate**—Li_2CO_3—are difficultly soluble in water; therefore they are precipitated from solutions of lithium salts by sodium phosphate or carbonate. By strong ignition the carbonate loses carbon dioxide. So far as these two salts are concerned, lithium approaches the metals of the calcium group (p. 278). Its compounds color the flame a beautiful red; the spectrum shows an intense red line.

AMMONIUM COMPOUNDS.

Upon page 129 we observed that ammonia combines directly with the acids to form salt-like compounds, which are analogous to the metallic salts, especially those of potassium. The monovalent group, NH_4, playing the rôle of metal in these derivatives, is called *ammonium*, and the derivatives of ammonia, ammonium compounds. The metallic character of the group NH_4 is confirmed by the existence of *ammonium amalgam*, which, as regards its external appearance, is very similar to the sodium and potassium amalgams. Ammonium amalgam may be prepared by letting the electric current act upon ammonium chloride, NH_4Cl, viz., by immersing the negative platinum electrode into a depression in the ammonium chloride, which is filled with mercury. Then, as in the case of the decomposition of potassium or sodium chloride, a metal—ammonium—separates on the negative pole, and combines to an amalgam with mercury. The amalgam may also be obtained if sodium amalgam be covered with a concentrated solution of ammonium chloride:—

$$\underset{\text{Sodium amalgam.}}{(Hg + Na)} \text{ and } NH_4Cl \text{ yield } \underset{\text{Ammonium amalgam.}}{(Hg + NH_4)} \text{ and } NaCl.$$

Ammonium amalgam forms a very voluminous mass with a metallic appearance. It is very unstable, and decomposes rapidly into mercury, ammonia, and hydrogen.

On dissolving in water ammonia yields a strong alkaline solution; no proofs, however, exist which would lead us to accept the existence of ammonium hydroxide (NH_4OH) in the solution. On the other hand, there are organic derivatives of ammonium hydroxide, in which the hydrogen of the ammonium is replaced by hydrocarbon residues; *e. g.*, tetramethyl ammonium hydroxide—$N(CH_3)_4OH$. These are thick liquids, of strong basic reaction and, in all respects, are very similar to potassium and sodium hydroxides.

Ammonium Chloride—NH_4Cl—is sometimes found in volcanic districts, and was formerly obtained by the dry distillation of camel's dung (*Sal ammoniacum*). At present it is prepared almost exclusively by saturating the ammonia water from gas works with hydrochloric acid. The solution is evaporated to dryness, and the residue heated in iron vessels, when the ammonium chloride sublimes as a compact, fibrous mass. It dissolves in 2.7 parts of cold, and in one part of boiling water, and crystallizes from the solution in small, feather-like, grouped octahedra or cubes, of sharp, salty taste. When heated, ammonium chloride sublimes without melting; at the same time a dissociation into NH_3 and HCl is sustained, but these products recombine again to ammonium chloride, on cooling. The dissociation is complete at 350°, and the vapor density then equals 13.3 ($H = 1$), corresponding to that of a mixture of similar molecules, of NH_3 (8.5), and HCl (18.2). A like decomposition is sustained by the ammonium chloride when its solution is boiled; ammonia escapes and the solution contains some free hydrochloric acid.

Ammonium Sulphate—$(NH_4)_2SO_4$—is obtained by saturating the ammonia water from gas works with sulphuric acid. It crystallizes without water in rhombic prisms, and is soluble in two parts of cold and one part of hot water. It fuses at 140°, and by further heating decomposes into ammonia, nitrogen, water and ammonium sulphite.

Ammonium Nitrate—NH_4NO_3—is isomorphous with potassium nitrate and deliquesces in the air. When heated it melts at 159°, and then decomposes (about 86°) into hyponitrous oxide and water (p. 215).

Ammonium Nitrite—NH_4NO_2—is present in minute quantities in the air, and results from the action of the electric spark upon the latter when moist, and also in the oxidation of phosphorus. It may be obtained by the saturation of aqueous ammonia with nitrous acid—in a perfectly pure condition, by the decomposition of silver or lead nitrite by ammonium chloride. Heat decomposes it at 180° C., into nitrogen and water (p. 117).

The decomposition of ammonium nitrite into water and nitrogen, and ammonium nitrate into hyponitrous oxide and water are both exothermic reactions, occurring with the disengagement of heat (p. 302) :—

$$\underset{(88.1\ \text{Cal.})}{NH_4NO_3} = \underset{(2 \times 57.2\ \text{Cal.})}{2H_2O} + \underset{(-18.3.)}{N_2O} \ldots\ldots + 8.0\ \text{Cal.}$$

$$\underset{(64.9.)}{NH_4NO_2} = \underset{(2 \times 57.2\ \text{Cal.})}{2H_2O} + N_2 \ldots\ldots + 49.5\ \text{Cal.}$$

Consequently, these decompositions are not dissociations, but proceed independently of the pressure of the disengaged gas, and the components do not reunite to form their original compounds (p. 280).

Ammonium Carbonate.—The *neutral* or *secondary* salt $(NH_4)_2CO_3$, separates as a crystalline powder, when ammonia gas is conducted through a concentrated solution of the so-called sesquicarbonate. It parts with ammonia in the air and becomes the *primary* or *acid* salt, NH_4HCO_3, which, when heated to 58°, decomposes into carbon dioxide, ammonia, and water.

The common, commercial, so-called *sesquicarbonate of ammonium*, $(CO_2)_2(NH_3)_3.H_2O$, which can be regarded as a compound of primary ammonium carbonate with ammonium carbamate, $CO_3(NH_4)H + NH_2CO_2NH_4$ (see Organic Chemistry), arises in the decay of many nitrogenous carbon compounds, *e. g.*, the urine, and was formerly prepared by the dry distillation of bones, horn, and other animal substances. At present it is obtained by heating a mixture of ammonium chloride, or sulphate, with calcium carbonate. It then sublimes as a white, transparent, hard mass, which gives off ammonia and carbon dioxide in the air, falling into a white powder of primary ammonium carbonate. The latter, obtained by the efflorescence of the first two salts, or by saturating ammonium hydroxide with carbon dioxide, is a white, odorless powder, more insoluble in water. In aqueous solution it gradually loses carbon dioxide and is changed to the secondary carbonate.

Ammonium Phosphates.—The most important of these is the *secondary ammonium sodium phosphate*, $PO_4(NH_4)NaH + 4H_2O$, ordinarily termed *salt of phosphorus*. It is found in guano and decaying urine. It can be obtained by the crystallization of a mixture of di-sodium phosphate and ammonium chloride:—

$$Na_2HPO_4 + NH_4Cl = NH_4NaHPO_4 + NaCl.$$

It consists of large, transparent, monoclinic crystals. When heated it fuses, giving up water and ammonia and forms a transparent glass of sodium metaphosphate, $NaPO_3$ (p. 297). It serves in blow-pipe tests for the detection of various metals.

The *tertiary ammonium phosphate*—$(NH_4)_3PO_4$—separates upon mixing concentrated solutions of phosphoric acid and ammonia. Upon drying, it loses ammonia and passes into the *secondary salt*, $(NH_4)_2HPO_4$, which changes to the *primary salt*, $PO_4(NH_4)H_2$, when its solution is boiled.

Ammonium Sulphide—$(NH_4)_2S$—results upon mixing 1 volume of H_2S with 2 volumes of NH_3 at —18°. It is a white crystalline mass, dissociating, at ordinary temperatures, into NH_4HS and NH_3. It is obtained in aqueous solution by the saturation of an ammonium hydrosulphide solution with ammonia; and also seems to dissociate into its constituents. A higher heat (even at 45°) completely dissociates ammonium sulphide:—

$$(NH_4)_2S = \underset{\text{2 vols.}}{2NH_3} + \underset{\text{1 vol.}}{H_2S}.$$

Ammonium Hydrosulphide—NH_4SH—is produced upon conducting hydrogen sulphide into an alcoholic ammonia solution. It is dissociated when warmed; this is complete at 45°:—

$$NH_4SH = \underset{\text{1 vol.}}{NH_3} + \underset{\text{1 vol.}}{H_2S}.$$

It is obtained in aqueous solution by saturating aqueous ammonia with hydrogen sulphide. At first the solution is colorless, but becomes yellow on standing in contact with the air, owing to the formation of ammonium polysulphides—$(NH_4)_2S_n$. The so-called yellow ammonium sulphide is more simply obtained by the solution of sulphur in the colorless hydrosulphide. Both solutions are often employed in laboratories for analytical purposes.

Recognition of Ammonium Compounds.—All ammonium salts are volatile and decompose upon heating. The alkalies and other bases liberate ammonia from them, which is recognized by its odor and the blue color it imparts to red litmus paper. Platinum chloride produces a yellow crystalline precipitate of ammonio-platinum chloride, $PtCl_4.2NH_4Cl$, in solutions of ammonium chloride. Tartaric acid precipitates primary ammonium tartrate.

The heat of formation of the most important ammonium compounds corresponds to the following symbols:—

$$(N,H_3) = 11.9 \quad (NH_3Aq.) = 8.4 \quad (N,H_3,S,H) = 39.0$$
$$(N,H_4,Cl) = 75.8 \quad (N,H_4,Br) = 65.3 \quad (N,H_4,I) = 49.3$$
$$(NH_4,Cl,Aq.) = -3.8 \quad (NH_4,Br,Aq.) = -3.3 \quad (NH_4,I,Aq.) = -3.5$$
$$(N_2,H_8,S,O_4) = 282.1 \quad (N,H_4,N,O_3) = 88.1 \quad (N,H_4,N,O_2) = 64.9$$
$$NH_3,HCl = 41.9 \quad NH_3,HBr = 45.0 \quad NH_3,HI = 41.4$$

METALS OF THE SECOND GROUP.

Ca 40 Sr 87.5 Ba 137.
Be 9.10 Mg 24.38
Zn 65.5 Cd 112.1 Hg 200.4.

The second group of the periodic system (see table, p. 249) comprises chiefly the divalent metals, which form compounds of the type MeX_2, and in their entire deportment exhibit many analogies. Their special relations and analogies are more closely regulated by the law of periodicity. Beryllium and magnesium belong to the small periods whose members are similar but do not show complete analogy. Beryllium exhibits many variations from magnesium, and in many properties approaches aluminium; just as lithium attaches itself to magnesium (p. 278). The metals, calcium, strontium, and barium, constitute the second members of the three great periods, are among themselves perfectly homologous (p. 247), and in accord with their strong basic character, attach themselves to the alkali metals K, Rb, and Cs. Zinc, cadmium, and mercury, which correspond to them and constitute the second sub-group, really belong to the right, negative sides of the three great periods. They fall in with the heavy metals, are much less basic, and resemble the alkaline earth metals only in their combination types. In consequence of the double periodicity of the three great periods both sub-groups (Ca, Sr, Ba and Zn, Cd, Hg) exhibit many analogies to magnesium and beryllium.

GROUP OF THE ALKALINE EARTHS.

CALCIUM.	STRONTIUM.	BARIUM.
Ca = 40.	Sr = 87.5.	Ba = 137.

The metals of the group are termed alkaline earth metals, because their oxides attach themselves in their properties, on the one side to the oxides of the alkalies, upon the other to the real earths (alumina, etc.). They show the same gradation in properties as the elements of the potassium group, and, with respect to their atomic weights, bear the same relation to each other. With increase in atomic weight, their chemical energy and basicity become greater.* Barium decomposes water energetically, and oxidizes more readily than strontium and calcium. In accord with this, we find barium hydroxide a stronger base; it dissolves rather readily in water, does not decompose upon ignition, and absorbs carbon dioxide rapidly from the air. Barium carbonate is also very stable, fuses at a white heat, and only disengages a little carbon dioxide. Calcium hydroxide, on the other hand, dissolves with more difficulty in water, and when ignited, breaks up into water and calcium oxide; the carbonate also yields carbon dioxide when similarly treated. In its entire character, strontium stands between barium and calcium. All these affinity relations find full expression in the heat of formation of the corresponding compounds.

While the alkaline earth metals are similar to the alkalies in their

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* See p. 255.

free condition and in their hydroxides, they essentially distinguish themselves from them by the insolubility of their carbonates and phosphates, and still more by their sulphates. Barium sulphate is almost insoluble in water and acids, while that of calcium dissolves in 400 parts water; strontium sulphate occupies an intermediate position.

The metals of this group do not form volatile compounds and their specific heats have not yet been determined. As the determination of the vapor densities of the elements or their volatile compounds, and the ascertainment of the specific heat of the metals, afford the only two direct means for the derivation of the true atomic weights, it was allowable to make the atomic weights of the calcium group equal to their equivalent weights ($Ca = 19.9, \overset{I}{Ca}Cl$). But the great analogy of their compounds to those of the metals of the magnesium group, their isomorphism for instance, argues with great probability for the divalence of the metals of the group, and that the present accepted double atomic weights are correct (compare p. 263). For calcium, this conclusion has already been confirmed by the experimental determination of its thermal capacity.

CALCIUM.

$Ca = 40.$

Calcium belongs to the class of elements most widely distributed upon the earth's surface. As calcium carbonate (limestone, marble, chalk) and the sulphate (gypsum, alabaster), it represents immense deposits in all stratified formations. As phosphate, it constitutes *phosphorite*, as fluoride, *fluorite*, both of which are abundant. As silicate, it is found in most of the oldest crystalline rocks.

The metal is obtained by the electrolysis of the fused chloride; further, by heating calcium iodide with sodium, or calcium chloride with sodium and zinc. Although the affinity of calcium for oxygen is less than that of the alkalies, yet the oxide (also BaO and SrO) cannot be reduced to metal by ignition with carbon, iron, or sodium —due, probably to the non-fusibility of the oxide.

Calcium is a yellow, shining metal, of specific gravity 1.55–1.6. In dry air it is tolerably stable, in moist it covers itself with a layer of hydroxide. It decomposes water with considerable energy. It fuses at a red heat, and in the air burns with a brilliant yellow light.

Calcium Oxide—Lime—CaO—may be obtained pure by igniting the nitrate or carbonate. It is prepared on a large scale by burning the ordinary limestone or marble ($CaCO_3$) in lime-kilns. It is a grayish-white mass, which does not fuse at the highest temperatures. The oxy-hydrogen flame thrown upon a piece of lime causes it to emit an extremely intense white light (Drummond's Lime Light). In the air lime attracts moisture and CO_2, becoming calcium carbonate; burned lime unites with water with evolution of much heat, breaking up into a white voluminous powder of calcium hydroxide $Ca(OH)_2$—*slaked lime.*

When limestone contains large quantities of alumina, magnesium carbonate, or other constituents, the lime from it slakes with difficulty, and is known as *poor* lime, to distinguish it from pure *fat* or *rich* lime, which is readily converted into a powder with water.

Calcium Hydroxide—$Ca(OH)_2$—slaked lime—is a white, porous powder, forming a thick paste, milk of lime, with water. It dissolves with difficulty in cold water (1 part in 760 parts), but with still more difficulty in warm water; the solution saturated in the cold (lime water) becomes cloudy upon warming. It has a strong alkaline reaction. In the air it attracts carbon dioxide and forms calcium carbonate. At a red heat it decomposes into oxide and water.

Slaked lime is employed in the preparation of ordinary mortar, a mixture of calcium hydroxide, water and sand. The hardening of the mortar in the air depends mainly upon the fact that the calcium hydroxide combines with the CO_2 of the air to form the carbonate, and at the same time acts upon the silicic acid of the sand forming a calcium silicate, which, in time, imparts durability to the mortar.

Hydraulic mortar, or cement, is produced by gently igniting a mixture of limestone or chalk with aluminium silicate (clay) and quartz powder. On stirring the powdered, burnt mass with water it soon hardens, and is not dissolved by water. Some naturally occurring limestones, containing upwards of 20 per cent. clay, yield hydraulic cements, without any admixtures after burning. Their composition varies, and also the process of their hardening; it however depends principally upon the formation of calcium and aluminium silicates.

Calcium Peroxide—CaO_2—is precipitated as a hydrate in crystalline leaflets, if lime water be added to a solution of barium peroxide in dilute hydrochloric acid; it is very unstable. It contains $8H_2O$, which it gradually loses in dry air.

The halogen derivatives of calcium, like those of other metals, are prepared by the solution of the oxide or carbonate in the haloid acids. They are formed by the direct union of calcium with the halogens; calcium burns in the vapors of chlorine, bromine and iodine. Technically, calcium chloride is often obtained as a by-product, *e. g.*, in the preparation of ammonia.

Calcium Chloride—$CaCl_2$—crystallizes from aqueous solution with 6 molecules of H_2O, in large, six-sided prisms, which deliquesce in the air. *In vacuo* it loses 4 molecules of H_2O. When heated, it melts in its water of crystallization, loses water, but it is only after it has been exposed above 200° that it becomes anhydrous; then it is a white, porous mass. The dry salt fuses at 719°, and solidifies to a crystalline mass, which attracts water energetically, and may be employed in the drying of gases and liquids. The dry calcium chloride also absorbs ammonia, forming the compound $CaCl_2.8NH_3$. The crystallized hydrous salt dissolves in water with reduction of temperature; by mixing with snow or ice the temperature is lowered to —48°. Upon fusing the dry chloride in air it will partially decompose into the oxide and hydrogen chloride.

Calcium bromide and iodide are very similar to the chloride.

Calcium Fluoride—$CaFl_2$—occurs in nature as *fluorite*, in large cubes or octahedra, or even in compact masses. It is often discolored by impurities. It is found, in sparing quantities, in the ashes of plants, bones and the enamel of the teeth. A soluble fluoride added to the solution of calcium chloride throws down insoluble calcium fluoride as a white voluminous precipitate.

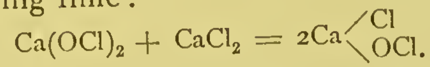
The fluoride is perfectly insoluble in water, and is only decomposed by strong acids. It fuses easily at a red heat, serving, therefore, as a flux in the smelting of ores. When heated it phosphoresces.

Calcium Hypochlorite—$Ca(ClO)_2$—is not known in a pure condition. The so-called *bleaching lime* or *chloride of lime*, obtained by conducting chlorine, at ordinary temperatures, over slaked lime, contains calcium hypochlorite as active principle.

According to analogy to the action of chlorine upon potassium, or sodium hydroxide, the reaction in the case of calcium hydroxide may be expressed by the following equation:—

$$2Ca(OH)_2 + 2Cl_2 = Ca(OCl)_2 + CaCl_2 + 2H_2O.$$

This would incline us to regard chloride of lime as a mixture of calcium hypochlorite, calcium chloride, and water. In accordance with the equation, the completely chlorinated chloride of lime must contain 48.9 per cent. chlorine, which is never the case, because a portion of the calcium hydroxide invariably remains unaltered. Calcium chloride does not exist free in bleaching lime, because it is not withdrawn from the latter by alcohol, and nearly all the chlorine of the bleaching lime can be expelled by carbon dioxide. It is therefore probable that the compound, $\mathrm{Ca}\left\langle\begin{matrix}\mathrm{Cl}\\ \mathrm{OCl}\end{matrix}\right.$ (Odling and Lunge), is present in bleaching lime:—



$$\mathrm{Ca(OCl)_2 + CaCl_2 = 2Ca}\left\langle\begin{matrix}\mathrm{Cl}\\ \mathrm{OCl}.\end{matrix}\right.$$

Chloride of lime is a white, porous powder with an odor resembling that of chlorine. The aqueous solution has a strong alkaline reaction, and bleaches. It decomposes in the air as the carbon dioxide of the latter liberates hypochlorous acid. Even in closed vessels it gradually breaks up, with elimination of oxygen; the decomposition is hastened by sunlight and heat, and may occur with explosion. Hence chloride of lime should be preserved in loosely closed vessels, in a cool dark place.

Dilute hydrochloric or sulphuric acid will expel chlorine from chloride of lime; the quantity liberated is just twice that which the hypochlorite eventually found in it contains:—

$$\mathrm{Ca(ClO)_2 + 4HCl = CaCl_2 + 2H_2O + 2Cl_2}.$$

When sulphuric acid acts, the calcium chloride present participates in the reaction:—

$$\mathrm{Ca(ClO)_2 + CaCl_2 + 2H_2SO_4 = 2CaSO_4 + 2Cl_2 + 2H_2O}.$$

The application of chloride of lime for the production of chlorine in chlorine bleaching and disinfection is based on this deportment.

The quantity of chlorine set free by acids from the chloride of lime represents its quantity of so-called *active chlorine;* good chloride of lime should contain at least 25 per cent.

Calcium chlorate and chloride are produced when the aqueous solution of chloride of lime is boiled:—

$$\mathrm{3Ca(ClO)_2 = (ClO_3)_2Ca + 2CaCl_2}.$$

On this is based the application of chloride of lime for the production of potassium chlorate ($\mathrm{KClO_3}$) by a transposition of calcium chlorate with potassium chloride.

When a small quantity of cobaltic oxide is added to the solution of bleaching lime, and heat applied, a regular stream of oxygen is disengaged; this is an advantageous method of preparing oxygen. Other oxides, like those of manganese, copper, and iron, behave similarly. In this reaction there occurs, apparently, a contact action of the oxides. The reaction is explained, doubtless, in the same way as the action of hydrogen peroxide upon certain oxides (see p. 103). The feebly combined oxygen atom in cobaltic oxide unites with the oxygen of the calcium hypochlorite to form free oxygen:—

$$\mathrm{Ca(ClO)_2} + \underset{\text{Cobaltic oxide.}}{\mathrm{2Co_2O_3}} = \mathrm{CaCl_2 + 2O_2} + \underset{\text{Cobaltous oxide.}}{\mathrm{4CoO}}.$$

The resulting cobaltous oxide is again converted by the chloride of lime into cobaltic oxide, which acts upon a fresh quantity of bleaching lime.

On warming bleaching lime with ammonia, the following decomposition occurs:—

$$3CaOCl_2 + 2NH_3 = 3CaCl_2 + 3H_2O + 2N.$$

This reaction can be used for the preparation of nitrogen.

Calcium Sulphate—$CaSO_4$—is very abundant in nature. In an anhydrous condition it forms the mineral *anhydrite*, crystallizing in forms of the rhombic system. With two molecules of water it occurs as gypsum, in large monoclinic crystals or in granular, crystalline masses (Alabaster, etc.). It also separates as a fine crystalline powder, $CaSO_4 + 2H_2O$, when soluble calcium salts are precipitated with sulphuric acid. Calcium sulphate dissolves with difficulty in water; 1 part at average temperatures is soluble in 400 parts H_2O. When heated to 110° gypsum loses all its water, and becomes *burnt* gypsum; when this is pulverized and mixed with water, it forms a paste which hardens to a solid mass in a short time. The hardening is dependent upon the reunion of anhydrous calcium sulphate with 2 molecules of H_2O. On this depends the use of burned gypsum for the production of moulds, figures, etc. In case gypsum has been too intensely heated (above 160°, dead-burnt gypsum) it will no longer harden with water; the naturally occurring anhydrite behaves in the same manner.

Calcium Nitrate—$Ca(NO_3)_2$—is produced by the decay of the nitrogenous organic substances in the presence of lime, therefore, it is frequently found as an efflorescence upon walls (in cattle stables). It crystallizes from water in monoclinic prisms, having four molecules of water; the anhydrous salt deliquesces in the air. By the action of potassium carbonate or chloride, calcium nitrate may be transposed into potassium nitrate (p. 285).

Calcium Phosphates. The *tertiary* phosphate—$Ca_3(PO_4)_2$—is found in slight quantities in most of the mountain rocks. In combination with calcium fluoride, it crystallizes as *apatite.* As phosphorite, it forms compact masses, more or less intimately mixed with other constituents, and occurs in immense deposits in Spain, France, Germany, and Russia. When these minerals disintegrate the calcium phosphate passes into the soil, and is absorbed by the plants. In the latter, it accumulates chiefly in the seeds and grains. In the animal kingdom, it is principally found in the bones, the ashes of which contain upwards of 85 per cent. calcium phosphate. Tertiary calcium phosphate is perfectly insoluble in water. If disodium phosphate be added to the aqueous solution of a calcium salt, and then ammonium hydroxide, it will separate as a gelatinous precipitate, which, after drying, becomes a white amorphous powder. It is very readily soluble in acids, even acetic.

The *secondary* calcium phosphate—$PO_4CaH + 2H_2O$—is sometimes present in guano, in the form of small, shining prisms, and separates as an amorphous precipitate, if disodium phosphate be added to a solution of calcium chloride mixed with some acetic acid. When ignited, it passes into calcium pyrophosphate, $P_2O_7Ca_2$.

The *primary* phosphate—$Ca(H_2PO_4)_2$—is produced by the action of sulphuric or hydrochloric acid upon the first two phosphates. It is readily soluble in water, and deliquesces in the air. Heated to 200°, it decomposes into pyrophosphate, metaphosphoric acid and water:—

$$2Ca(H_2PO_4)_2 = Ca_4P_2O_7 + 2HPO_3 + 3H_2O.$$

When intensely ignited, pure calcium metaphosphate remains (p. 135).

Calcium phosphate is present in all plants. Its presence in the soil is, therefore, an indispensable condition for its fertility. When there is a scarcity of phosphoric acid it must be added. To this end, bone meal and pulverized phosphorite were formerly employed. Since, however, the phosphoric acid is contained in these substances as tri-calcium phosphate, which is not easily absorbed by the plants, the primary phosphate is extensively employed at present as a fertilizer, or, better, the mixture resulting from the action of sulphuric acid upon the tertiary salt. Superphosphate is the name applied to the resulting mass. The Thomas slag, obtained in the dephosphorization of iron ores by the Gilchrist-Thomas process, constitutes a very valuable and important crude product from which to prepare calcium phosphate.

Calcium Carbonate—$CaCO_3$—is very widely distributed in nature. It crystallizes in two crystallographic systems, hence is dimorphous. In rhombic crystals, with the specific gravity 3.0, it forms aragonite. In hexagonal rhombohedra, with specific gravity 2.7, it occurs as calcite. Iceland spar, employed for optical purposes, is perfectly pure, transparent calcite. The common calcite, which constitutes immense mountain chains, is an amorphous or indistinct crystalline stratum, and is usually mixed with other constituents, as clay. When the limestone is granular and crystalline, it is termed marble. Dolomite also constitutes large layers, and is a compound of calcium and magnesium carbonates, with generally an excess of the former. *Chalk* is very pure amorphous calcium carbonate, consisting of the shells of microscopic sea animals. Calcium carbonate is, further, a regular constituent of all plants and animals; the shells of eggs, of mussels, even corals and pearls, consist chiefly of it.

A soluble carbonate, added to the aqueous solution of a calcium salt, precipitates calcium carbonate as a white, amorphous powder, which soon becomes crystalline. In the cold, it assumes the form of calcite; upon boiling the liquid, it generally changes into aragonite crystals.

The carbonate is almost insoluble in pure water; but dissolves somewhat in water containing carbon dioxide, as it very probably is changed to the *primary* carbonate—$Ca(HCO_3)_2$. For this reason, we find calcium carbonate dissolved in all natural waters. When the solution stands exposed, or if it be heated, carbon dioxide escapes, and the secondary carbonate again separates out. The formation of lime scales, thermal tufts, stalactites, boiler scales and similar deposits are due to this. Calcium carbonate, like all carbonates, is decomposed by acids, with evolution of carbon dioxide. At a red heat, it dissociates into CaO and CO_2. The change begins at 600°. The tension of dissociation is 85 mm. at 860°, and at 1040° 510–520 mm. For this reason calcium carbonate is not decomposed when heated in a sealed tube.

Calcium Silicate—$CaSiO_3$—occurs as white, crystalline wollastonite. It is also a constituent of most natural silicates and of the artificial silicate fusion—glass.

Glass.—The silicates of potassium and sodium are readily fusible and soluble in water. The silicates of calcium and the other alkaline earths are insoluble, very difficultly fusible, and generally crystallize when they cool. If, however, the two silicates be fused together, an amorphous, transparent mass, of average fusibility, results; it is only slightly attacked by water and acids—it is glass. To prepare the latter, a mixture of sand, lime, and soda, or potash, is heated to fusion in a muffle furnace. Instead of the carbonates of potassium and sodium a mixture of sulphates with charcoal can be employed; the carbon reduces the sulphates to sulphides, which form silicates when fused with silicon dioxide.

The following are the varieties of glass:—

Soda Glass—a mixture of sodium and calcium silicates—fuses readily, and is employed for window-panes and ordinary glass vessels. *Potash* or *Bohemian Glass*, also called Crown Glass, consists of calcium and potassium silicates, is not very fusible, is harder and withstands the action of water and acids better than soda glass; it is, therefore, employed in the manufacture of chemical glassware.

Glass Crystal or *Flint Glass* is composed of potassium and lead silicates. It is not as hard, fuses with tolerable readiness, refracts light strongly, and when polished, acquires a clear lustre. On this account it is employed for optical purposes (for lenses, prisms) and is used in ornamental glassware. *Strass*,—a lead glass containing boron trioxide, is used to imitate precious stones. The opaque varieties of enamel consist of lead glass and in the fused glass are insoluble admixtures, as tin dioxide and calcium phosphate.

Ordinary window glass is obtained by the fusion of rather impure materials; in consequence of the presence of ferrous oxide it is ordinarily colored green. To remove this coloration, manganese peroxide, MnO_2, is added to the fusion. It oxidizes a portion of the ferrous to ferric oxide, the silicate of which is colored slightly yellow, while manganese forms a violet silicate. These colors, violet and green, almost neutralize each other as complementaries. The colored glasses contain silicates of colored metallic oxides; chromic and cupric oxides color green; cobaltic, blue; cuprous oxide, a ruby red, etc.

The sulphur compounds of calcium are very much like those of the alkalies. **Calcium Sulphide**—CaS—is most readily obtained by heating the sulphate with carbon, and is a whitish-yellow mass. When it is dissolved in water we get **Calcium Hydrosulphide**

—$Ca(SH)_2$—which decomposes on boiling the aqueous solution. When calcium oxide is ignited with sulphur in a closed crucible a yellowish-gray mass is obtained, which consists of calcium polysulphides and sulphate. Milk of lime boiled with sulphur yields a deep, yellow solution of calcium polysulphides. When the solutions of the latter are acted upon by acids, finely divided sulphur —milk of sulphur—is precipitated and H_2S set free. If the reverse occur, viz., the addition of a solution of polysulphides to an excess of dilute acids, hydrogen persulphide will separate (p. 111).

STRONTIUM.

$Sr = 87.5$.

This element is rather rare in nature, and is principally found in strontianite (strontium carbonate) and celestite (strontium sulphate). Its compounds are very similar to those of calcium.

The metal is obtained by the electrolysis of fused strontium chloride. It has a brass-yellow color, and a specific gravity, 2.5. It oxidizes in the air and burns with a bright light when heated. It decomposes water at the ordinary temperatures.

Of the compounds of strontium we may mention the following:—

Strontium Oxide—SrO—is most readily obtained by igniting the nitrate. It unites with water, with strong evolution of heat, forming **Strontium Hydroxide**—$Sr(OH)_2$—which is more readily soluble in water than calcium hydroxide. It crystallizes from aqueous solution with 8 or 9 molecules of H_2O. When ignited it decomposes into SrO and H_2O, but with more difficulty than calcium hydroxide.

Strontium Chloride—$SrCl_2 + 6H_2O$—crystallizes from water in hexagonal tables, which deliquesce in the air; it is somewhat soluble in alcohol.

Strontium Sulphate—$SrSO_4$—is much more difficultly soluble in water than calcium sulphate, but is not as insoluble as barium sulphate.

Strontium Nitrate—$Sr(NO_3)_2$—is obtained by dissolving the carbonate in nitric acid, and is readily soluble in water, but insoluble in alcohol. It crystallizes from warm solutions in anhydrous octahedra, but from cold, with 4 molecules of H_2O, in monoclinic prisms. Mixed with combustible substances it colors the flame a beautiful carmine red, and for this reason is employed in pyrotechny.

Strontium Carbonate—$SrCO_3$—is precipitated from aqueous solutions of strontium salts by soluble carbonates, as an amorphous, insoluble powder. When ignited it breaks up into SrO and CO_2. This decomposition does not, however, occur so easily as with calcium carbonate.

BARIUM.

$Ba = 137$.

Barium occurs in nature in large masses, as heavy spar (or barium sulphate), and as witherite (barium carbonate). All its compounds are distinguished by their high specific gravity, hence the name barium, from βαρὺς, heavy. In accordance with its general character, barium is a stronger basic metal than either strontium or calcium (p. 303).

The barium salts are either prepared from the natural witherite, by dissolving it in acids, or from heavy spar. The latter is almost insoluble in all acids; to obtain the other compounds from it, it must first be converted into sulphide. For this purpose a mixture of barium sulphate and carbon is heated to redness, whereby the sulphate is reduced to sulphide, which is soluble in water and readily transposed by acids.

Metallic barium was first obtained by the electrolysis of the fused chloride. The following method is more convenient: Sodium amalgam is added to a hot saturated barium chloride solution; the sodium displaces the barium, which forms an alloy with the mercury. The resulting liquid barium amalgam is kneaded with water, to remove all the sodium, and then heated in a stream of hydrogen, to volatilize the mercury.

Barium is a bright yellow metal, of specific gravity, 3.6. It fuses at a red heat, but does not vaporize. It is rapidly oxidized in the air; like sodium it decomposes water very energetically, even at ordinary temperatures.

Barium Oxide—BaO—is obtained by the ignition of barium nitrate. It is a gray, amorphous mass, of specific gravity, 5.5, and fusible in the oxy-hydrogen flame. With water it yields the hydroxide, with evolution of much heat.

Barium Hydroxide—$Ba(OH)_2$—is precipitated from concentrated solutions of barium salts by potassium or sodium hydroxide, not, however, by ammonium hydroxide. At ordinary temperatures it dissolves in 20 parts, upon boiling, in 3 parts water. From aqueous solution it crystallizes with 8 molecules of H_2O in four-sided prisms or leaflets. The solution—called *Baryta water*—is strongly alkaline and is very similar to the alkalies. When exposed to the air it absorbs carbon dioxide and becomes turbid, with separation of barium carbonate. At a red heat it fuses without decomposition like the caustic alkalies, and solidifies to a crystalline mass.

Barium Peroxide—BaO_2—is produced when barium oxide is heated in a stream of air or oxygen, and always contains oxide. To purify it, the commercial peroxide is rubbed together with water and added to a very dilute hydrochloric acid, until the latter is almost saturated. An excess of baryta water is added to the solution, containing barium chloride and hydrogen peroxide, when *hydrated barium peroxide*—$BaO_2 + 8H_2O$—separates in shining scales, which, upon warming, readily lose water and break up into a white powder consisting of barium peroxide. The latter is a compact gray mass when obtained directly from the oxide.

The peroxide dissolves in dilute acids, with production of hydrogen peroxide. Concentrated sulphuric acid sets free ozonized oxygen from it. When strongly ignited (above 400°) it decomposes into barium oxide and oxygen.

Barium Chloride—$BaCl_2$—crystallizes from aqueous solution, with two molecules of H_2O, in large, rhombic tables, which are stable in the air. It dissolves readily in water, and is poisonous, like all soluble barium salts.

Barium Nitrate—$Ba(NO_3)_2$—crystallizes in anhydrous, shining octahedra, of the regular system, soluble in 12 parts of cold and 3 parts of hot water. It is employed as a green fire in pyrotechny.

Barium Sulphate—$BaSO_4$—is found in nature as heavy spar, in rhombic prisms, with a specific gravity of 4.6. It is obtained artificially by the precipitation of barium salts with sulphuric acid in the form of a white, amorphous powder, almost insoluble in water and acids. Under the name of *permanent white*, it is used as a paint, as a substitute for poisonous *white lead*, from which it is also distinguished by its unalterability.

Barium Carbonate—$BaCO_3$—as witherite, occurs in shining, rhombic crystals, and is precipitated from barium solutions by soluble carbonates, as a white, amorphous powder. It fuses at a white heat, and loses some carbon dioxide.

Barium Sulphide—BaS—is obtained by igniting the sulphate with carbon. It dissolves in water, with decomposition into hydroxide and hydrosulphide.

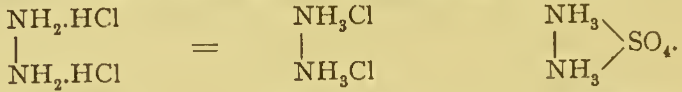
RECOGNITION OF THE COMPOUNDS OF THE ALKALINE EARTHS.

The carbonates and phosphates of this group are insoluble in water; hence are precipitated from the aqueous solutions of their salts upon the addition of soluble carbonates and phosphates (of the alkalies). The sulphates are also insoluble in acids (only calcium sulphate is somewhat soluble); for this reason they are thrown down from acid solutions by soluble sulphates or free sulphuric acid; the precipitation is complete, even with calcium, if alcohol be added to the solution. The hydroxides of the alkaline earths, which are more or less soluble in water, are only precipitated by sodium or potassium hydroxide from concentrated solutions. In solutions of barium salts hydrofluosilicic acid produces a crystalline precipitate of barium silicofluoride, $BaSiFl_6$.

The flame colorations produced by the volatile compounds are very characteristic; calcium salts impart a reddish-yellow color; strontium, an intense crimson; barium, a yellowish-green. The spectra correspond to these flame colors. The spectrum of calcium exhibits several yellow and orange lines, and in addition, a green and a violet line (see the spectrum table); that of strontium contains, besides several red lines, an orange and a blue, which are less distinct but very characteristic. Finally, the barium spectrum consists of several orange, yellow, and green lines, of which a bright green is particularly prominent.

DIAMMONIUM COMPOUNDS.

Hydrazine, N_2H_4, mentioned p. 132, bears the same relation to the divalent alkaline earth metals that ammonia bears to the univalent alkali metals (p. 299). It combines with two equivalents of acids to yield compounds, which must be regarded as salts of the divalent metallic diammonium, $H_3N.NH_3$:—



$$\begin{array}{c} NH_2.HCl \\ | \\ NH_2.HCl \end{array} = \begin{array}{c} NH_3Cl \\ | \\ NH_3Cl \end{array} \qquad \begin{array}{l} NH_3\diagdown \\ | \qquad SO_4. \\ NH_3\diagup \end{array}$$

Diamide Hydrochloride. Diammonium Chloride. Diammonium Sulphate.

The similarity of hypothetical diammonium to the alkaline earth metals is shown in the insolubility of its sulphate.

Diammonium Chloride, $N_2H_4(HCl)_2$, hydrazine hydrochloride, is obtained from the sulphate by transposition with barium chloride. It is very readily soluble in cold water, consists of large isometric crystals, and melts with decomposition at about 200°.

Diammonium Sulphate, $N_2H_4.SO_4H_2$, hydrazine sulphate, dissolves with difficulty in cold water, and crystallizes in vitreous plates. It deflagrates when exposed to a strong heat.

The powerful reducing property of the hydrazine compounds is characteristic of them. They precipitate metallic silver from an ammoniacal silver nitrate solution, and cuprous oxide and metallic copper from an alkaline copper solution (Fehling's solution).

METALS OF THE MAGNESIUM GROUP.

In this group are usually included beryllium, magnesium, zinc, and cadmium. However, these metals do not exhibit complete analogy, as is clearly seen in the periodic system (p. 302). Beryllium shows the greatest variations. It approaches aluminium, while magnesium resembles not only zinc and cadmium, but also the alkaline earth-metals, calcium, strontium, and barium. Its similarity to the latter is expressed by the basic nature of its oxide, whereas it resembles zinc and cadmium mainly in isomorphism of compounds.

Beryllium and magnesium bear the same relation to Ca, Sr, and Ba, as lithium and sodium bear to the metals of the potassium group.

The alkaline character of the alkaline earth-metals gradually diminishes from barium to calcium, and becomes almost nothing in magnesium and beryllium, which possess the lowest atomic weights (see p. 302). Magnesium and beryllium are scarcely capable of decomposing water, even at boiling temperatures. Their oxides and hydroxides are almost insoluble in it; the hydroxides decompose, on gentle ignition, into oxides and water. Their carbonates are very unstable; their chlorides, too, suffer a partial decomposition into oxide and hydrogen chloride, even on drying. The solubility of the sulphates of magnesium and beryllium further distinguishes them from the metals of the alkaline earth group.

The specific properties of beryllium and magnesium are maintained in zinc and cadmium, which constitute a natural group with the former. Zinc and cadmium do not decompose water at a boiling heat; their hydroxides are insoluble in it, and are not very stable; their carbonates and chlorides easily undergo decomposition; their sulphates are readily soluble in water. The similarity is further expressed by the isomorphism of most of their compounds. Thus, magnesium and zinc sulphates crystallize with 7 molecules of H_2O, in perfectly similar forms. If the solution of a mixture of both salts be allowed to crystallize, we get crystals with variable quantities of zinc and magnesium: the formation of such *isomorphous mixtures* in *ad libitum* proportions, is a characteristic indication of the isomorphism of compounds chemically similar.

The difference between beryllium and magnesium upon the one side, and zinc and cadmium on the other, is shown distinctly in their specific gravities. While the first two elements possess a low specific gravity (Be—2.1, Mg—1.75), zinc and cadmium (with specific gravities 7.2 and 8.6) belong to the so-called heavy metals (see p. 259).

The difference in specific gravity determines, also, many differences in chemical character. The light metals (especially the alkalies and alkaline earths) form rather unstable sulphides, readily soluble in water, while the sulphides of zinc and cadmium, like those of all heavy metals, are insoluble in water, and, usually, in acids; in these respects, magnesium and beryllium behave like the alkalies, while zinc and cadmium are precipitated by hydrogen sulphide or alkaline sulphides as sulphides from solutions of their salts. Further, the oxides of the light metals are very stable, and are only reduced by carbon if they are readily fusible (like potassium and sodium oxides); the heavy metals, on the other hand, are easily separated from their oxides by carbon. Zinc and cadmium oxides are reduced by carbon, while those of magnesium and beryllium are not altered. See further, p. 255. All these affinity relations are more clearly expressed and explained in their thermo-chemical relations (p. 323).

MAGNESIUM.

$Mg = 24.38.$

Magnesium is abundant in nature, and almost always accompanies calcium in its compounds. As carbonate, it occurs in compact masses, as magnesite, etc. Dolomite, which forms entire mountains, is an isomorphous mixture of calcium and magnesium carbonates. Magnesium is also present in most of the natural silicates; its soluble salts are contained in almost all natural waters.

Metallic magnesium may be obtained by the electrolysis of the chloride, or by heating the same with sodium. It was formerly prepared by heating the double chloride of magnesium and sodium with metallic sodium and fluorspar, the latter serving merely as a flux:—

$$MgCl_2.NaCl + 2Na = 3NaCl + Mg.$$

At present magnesium is obtained in large quantities by the method of Grätzel, which consists in electrolyzing the chloride, heated to fusion in crucibles.

Magnesium is a brightly shining, almost silver-white metal, of specific gravity 1.75. It is tenacious and ductile, and when heated may be converted into wire and rolled out into thin ribbons. It melts at about 800°, and distils at a bright-red heat. At ordinary temperatures, it scarcely oxidizes in the air; it burns, when heated, with an extremely intense white light, owing to the glowing non-volatile magnesium oxide. Magnesium light is rich in chemically active rays, and, for this reason, it is employed for photographing in dark chambers. Its alloy with zinc is generally employed as a substitute for pure magnesium, as it burns with an equally bright light. Boiling water is very slowly decomposed by magnesium. It dissolves easily in dilute acids, forming salts; the alkalies do not attack it.

Magnesium Oxide—MgO—or magnesia, formed by the combustion of magnesium, is ordinarily obtained by the ignition of the hydroxide or the carbonate (*magnesia usta*). It is a white, very voluminous, amorphous powder, which finds application in medicine. The feebly ignited magnesia combines with water, with slight generation of heat, to produce magnesium hydroxide.

Magnesium Hydroxide—$Mg(HO)_2$—is precipitated from solutions of magnesium salts by potassium or sodium hydroxide as a gelatinous mass. Dried at 100° it is a white amorphous powder. It is almost insoluble in water and alkalies; moist litmus paper is, however, colored blue. Ammonium salts dissolve it quite easily, forming soluble double salts. Magnesium hydroxide attracts carbon dioxide from the air and forms magnesium carbonate. It yields the oxide and water when gently ignited.

Magnesium Chloride—$MgCl_2$—is present in traces in many mineral springs. It may be prepared by the solution of the carbonate or oxide in hydrochloric acid; in large quantities it is obtained as a by-product in the technical production of potassium chloride. When its solution is evaporated the salt crystallizes out with six molecules of H_2O in deliquescent crystals, isomorphous with calcium chloride. When these are heated they give up water, and there occurs at the same time a partial decomposition of the chloride into oxide and hydrogen chloride:—

$$MgCl_2 + H_2O = MgO + 2HCl.$$

As magnesium chloride is produced in large quantities in various technical processes, repeated efforts have been made to utilize the above reaction for the preparation of hydrochloric acid, by conducting steam over heated magnesium chloride. However, the thermal relations of the reaction indicate that this could only be accomplished with difficulty. From the chemical affinities coming into play, the reaction pursues an opposite course, as the magnesium oxide is readily decomposed by hydrochloric acid into magnesium chloride and water:—

$$MgO + 2HCl = MgCl_2 + H_2O.$$

This is because the heat of formation of $MgCl_2$ (151.0 C.) and steam (58.0) is greater than that of MgO (145.8) and 2HCl (44.0). The decomposition is even easier in the presence of water, as is evident from the thermal numbers. The reverse reaction is, therefore, endothermic, requires the addition of chemical energy in the form of heat, and like all similar reactions is incomplete.

To get anhydrous magnesium chloride ammonium chloride is added to the solution of the former. The double salt, $MgCl_2.NH_4Cl + 6H_2O$, is formed. When this is heated it first loses water, and at 460° throws off ammonium chloride, leaving anhydrous magnesium chloride. This is a leafy, crystalline mass, which fuses at 708°, and distils undecomposed at a red heat; it is very deliquescent in the air.

Double salts, similar to the above, are also formed from potassium and calcium chloride. The potassium double salt—$MgCl_2.KCl + 6H_2O$—occurs in considerable deposits as carnallite at Stassfurt.

Magnesium Sulphate—$MgSO_4$—is found in sea-water and in many mineral springs. With more or less water it is *kieserite*, which abounds extensively at Stassfurt. At ordinary temperatures it crystallizes with 7 molecules of H_2O—$MgSO_4 + 7H_2O$—in four-sided rhombic prisms, readily soluble in water (at 0° in 2 parts water). It has a bitter, salt-like taste, and serves as an aperient. It crystallizes with 6 molecules of H_2O from solutions heated to 70°; at 0°, however, it has 12 molecules. When heated to 150° these hydrates lose all their water of crystallization, excepting *one molecule*, which escapes above 200°. *One* molecule of water, in magnesium sulphate is, therefore, more closely combined than the rest. Many other salts containing water deport themselves similarly. The more intimately combined water is termed *Water of Constitution.*

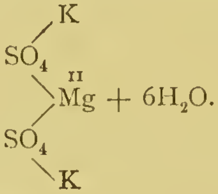
Magnesium sulphate forms double salts with potassium and ammonium sulphates, which crystallize with 6 molecules of H_2O in monoclinic prisms, *e.g.* :—

$$MgSO_4.K_2SO_4 + 6H_2O.$$

The sulphates of zinc and several other metals, *e.g.*, iron, cobalt, and nickel, in their divalent forms, are very similar to magnesium sulphate. Their sulphates crystallize with 7 molecules of H_2O, are isomorphous, and contain 1 molecule of intimately combined water. They form double salts with potassium and ammonium sulphates; these crystallize with $6H_2O$, and are isomorphous; *e.g.* :—

$$ZnSO_4 + 7H_2O \qquad ZnSO_4.K_2SO_4 + 6H_2O.$$
$$FeSO_4 + 7H_2O \qquad FeSO_4.K_2SO_4 + 6H_2O.$$

The constitution of these double salts may be viewed in the same way as that of potassium-sodium sulphate, or of mixed salts of polybasic acids. We may suppose that in the given instance the divalent metal unites two molecules of sulphuric acid :—



Magnesium Phosphates.—The *tertiary* phosphate $(PO_4)_2Mg_3$, accompanies the tertiary calcium phosphates in small quantities in bones and in plant ashes. The *secondary* phosphate, $MgHPO_4 + 7H_2O$, is precipitated from the soluble magnesium salts, by disodium phosphate (Na_2HPO_4) as a salt dissolving with difficulty in water. If ammonium salts be present, the precipitated double salt will be *magnesium ammonium phosphate*, $MgNH_4PO_4 + 6H_2O$, insoluble in water. The latter is found in guano, forms in the decay of urine, and is sometimes the cause of the formation of calculi. The *primary* salt, $H_4Mg(PO_4)_2$, has not been obtained.

The magnesium salts of arsenic acid, H_3AsO_4, are very similar to those of phosphoric acid. Magnesium-ammonium arseniate ($MgNH_4AsO_4 + 6H_2O$) is likewise almost insoluble in water.

Magnesium Carbonate, $MgCO_3$, occurs in nature as magnesium spar, crystallized in rhombohedra (isomorphous with calcite), in compact masses as magnesite. Combined with calcium carbonate, it forms dolomite, to which, when pure, is ascribed the formula, $CaCO_3.MgCO_3$; however, it usually contains an excess of calcium carbonate. On adding sodium or potassium carbonate to the aqueous solution of a magnesium salt, some carbon dioxide escapes, and a white precipitate forms, which consists of a mixture of magnesium carbonate and hydroxide. If the precipitate be dried at low temperature, we obtain a white, voluminous powder, whose composition generally corresponds to the formula $Mg(OH)_2.4CO_3Mg + 4H_2O$. This salt is employed under the name *Magnesia alba* in medicine.

If it be suspended in water, and carbon dioxide passed through it, the salt will dissolve, and upon standing exposed to the air, crystals of *neutral carbonate*, $MgCO_3 + 3H_2O$, separate. When these are boiled with water they give up carbon dioxide and are again converted into the basic carbonate. The naturally occurring magnesite sustains no change when boiled, and it is only when it is heated above 300° that it decomposes into MgO and CO_2.

Magnesium carbonate yields isomorphous double salts, with potassium and ammonium carbonate; *e. g.*, $MgCO_3.K_2CO_3 + 4H_2O$.

Of the *silicates* of magnesium, we may mention olivine (Mg_2SiO_4), serpentine ($Mg_3Si_2O_7 + 2H_2O$), talc ($Si_5O_{14}Mg_4$), sepiolite ($Si_3O_8Mg_2 + 2H_2O$), or meerschaum. The mixed silicates of magnesium and calcium are very numerous; to these belong asbestos, the augites and hornblendes.

Recognition of Magnesium Compounds.—The fixed alkaline hydroxides precipitate magnesium hydroxide from magnesium salts; the carbonates throw down basic magnesium carbonate. The precipitates are insoluble in pure water and the alkalies, but dissolve readily in solutions of ammonium salts. In the presence of the latter, neither the alkaline hydroxides nor carbonates cause precipitation. In presence of ammonium salts, disodium phosphate precipitates magnesium-ammonium phosphate, $MgNH_4PO_4 + 6H_2O$, insoluble in water.

BERYLLIUM.

$Be = 9.1$.

Among the metals of the second group beryllium occupies a position similar to that of lithium in the first group; in both elements, which have the lowest atomic weight in their group, the specific group character is considerably diminished, or does not find expression. As lithium attaches itself in many respects to magnesium, so does beryllium approach aluminium. Like the latter, it is scarcely at all attacked by nitric acid, but dissolves easily in sodium or potassium hydroxide, with elimination of hydrogen. Like aluminium oxide, that of beryllium dissolves in the alkalies, and is almost invariably accompanied by the former in its natural compounds. Beryllium sulphate, like that of aluminium, forms a difficultly soluble double salt with potassium sulphate. However, beryllium, in most of its compounds, stands nearer to magnesium than to aluminium. The determination of the vapor density of beryllium chloride (see below) has finally established the atomic weight and the valence of this element.

Beryllium is not very abundant in nature and is found principally in beryl, a double silicate of aluminium and beryllium—$Al_2Be_3(SiO_3)_6$. Emerald has the same composition, and is only colored green by a slight amount of chromium oxide.

Metallic beryllium is obtained by the ignition of the chloride with sodium, and is a white ductile metal, of specific gravity 1.64. Its specific heat equals 0.4084; the atomic heat is, therefore, 3.8 (p. 261). It does not decompose water, even upon boiling. It does not oxidize in the air at ordinary temperatures. When finely divided it will burn in the air with a very bright light when heated. In a compact mass (like magnesium), it does not do this. It is readily dissolved by dilute hydrochloric and sulphuric acids; also by potassium and sodium hydroxides.

Beryllium Chloride—$BeCl_2$—is obtained, like aluminium chloride, by the ignition of a mixture of beryllium oxide and carbon in a stream of chlorine. It sublimes in shining needles, which deliquesce in the air. Its vapor density equals 2.8 (air = 1) or 40.3 (H = 1) at 680–800° C., corresponding to the molecular formula $BeCl_2 = 79.9$ (Nilson.) It crystallizes from aqueous solution with four molecules of H_2O; upon drying it suffers a decomposition similar to that of magnesium chloride.

The salts of beryllium have a sweet taste, hence it has been called *glucinum.* Ammonium hydroxide precipitates a white, gelatinous *beryllium hydroxide,* $Be(OH)_2$, from solutions of the soluble salts. This dissolves readily in sodium and potassium hydroxide, but on boiling, separates again from solution. When heated, the hydroxide breaks up into water and *beryllium oxide,* BeO, which is a white, amorphous powder, of specific gravity 3.06. Its specific heat equals 0.2471.

Beryllium Sulphate—$BeSO_4$—crystallizes from water at various temperatures, with four or seven molecules of H_2O, of which one is rather closely combined. It crystallizes with magnesium sulphate in an isomorphous mixture. The double salt, $SO_4Be.SO_4K_2 + 3H_2O$, does not dissolve readily in water; in this respect it resembles the alums.

ZINC.

Zn = 65.5.

The natural compounds of the heavy metals have generally a high specific gravity, frequently possess metallic lustre, usually occur in the older crystalline rocks in veins, and are termed *ores.* The most important zinc ores are the carbonate—$ZnCO_3$—the silicate, and sphalerite or blende, ZnS. The principal sources of these ores are in Silesia, England, Belgium, Poland and the United States. To get the metal the carbonate or sulphide is converted into oxide by roasting in the air; the product is then mixed with carbon and ignited in cylindrical clay tubes. In this manner the oxide is reduced:—

$$ZnO + C = Zn + CO,$$

and the liberated zinc distilled off. The receivers contain the fused, compact zinc and a gray, pulverulent mass, called *zinc dust,* which consists of a mixture of zinc oxide with finely divided metal. This material is used in laboratories as a strong reducing agent.

Metallic zinc has a bluish-white color, and exhibits rough, crystalline fracture; its specific gravity equals 7–7.2. At ordinary temperatures it is brittle and can be pulverized; at 100–150° it is malleable and can be rolled into thin leaves and drawn out into wire. At 200° it becomes brittle again and may be easily broken. It fuses at 412° and distils about 1000°.

It becomes coated with a thin layer of basic carbonate in moist air. Heated in the air it burns to zinc oxide with a very intense, bluish-white light. Compact zinc will only decompose water at a red heat; zinc dust, however, acts at ordinary temperatures. Zinc is readily soluble in dilute acids, and dissolves with liberation of hydrogen in potassium or sodium hydroxide, as well as in ammonia, when the solutions are boiled.

Owing to its slight alteration in the air zinc meets with extensive application as sheet-zinc for coating statues and in architectural adornment, and in galvanizing sheet-iron. It also forms an important constituent of many valuable alloys, such as brass and argentan (see these).

Zinc Hydroxide—$Zn(OH)_2$—is precipitated as a white amorphous powder, from aqueous solution, by alkalies, and is soluble in excess of the reagent. When heated it decomposes into water and zinc oxide.

Zinc Oxide—ZnO—is usually prepared by igniting the precipitated basic carbonate, and, as *zinc white*, is employed as a stable white paint. The oxide obtained by burning the metal is a white, voluminous, flocculent mass, called *flores Zinci* or *Lana philosophica*. When zinc oxide is heated it acquires a yellow color, which disappears on cooling.

Zinc oxide occurs in nature as *zincite*, colored by impurities.

Zinc Chloride—$ZnCl_2$—anhydrous, is obtained by heating zinc in a stream of chlorine, by the evaporation of the solution of zinc in hydrochloric acid, and by the distillation of zinc sulphate with calcium chloride. It forms a white, deliquescent mass, which fuses when heated and distils about 680°. When the aqueous solution of zinc chloride is evaporated it partially decomposes (like magnesium chloride) into zinc oxide and hydrochloric acid. When the concentrated zinc chloride is mixed with zinc oxide, a plastic mass is obtained, which hardens rapidly; a mixture of magnesium chloride and oxide does the same. In both instances the hardening depends upon the formation of basic oxy-chlorides, *e. g.*, $ZnClOH$. Zinc chloride forms deliquescent double salts with the alkaline chlorides, *e. g.*, $ZnCl_2.2KCl$. With ammonia it yields various compounds, of which $ZnCl_2.NH_3$ is characterized by great stability.

Zinc Sulphate—$ZnSO_4$—is obtained by dissolving zinc in sulphuric acid. It is prepared upon a large scale by a gentle roasting of zinc blende (ZnS); the zinc sulphate is extracted by water. It crystallizes at ordinary temperatures from aqueous solutions with 7 molecules of H_2O (zinc or white vitriol) in rhombic crystals, resembling those of magnesium sulphate. It affords double salts with the alkaline sulphates; these contain 6 molecules of water (p. 308).

Zinc Carbonate—$ZnCO_3$—occurs native as smithsonite in hexagonal crystals, isomorphous with those of calcite. Sodium carbonate precipitates basic carbonates of varying composition from solutions of zinc salts.

Zinc Sulphide—ZnS—is zinc blende, usually colored brown by ferric oxide or other admixtures. Ammonium sulphide precipitates it as a white compound, from zinc solutions. Although fused zinc reacts with difficulty with sulphur, zinc dust combines with the latter in powdered form quite readily, and if the mixture be heated or struck with a hammer the union is accompanied by an explosion. Zinc sulphide is insoluble in water, but is readily dissolved by dilute acids, excepting acetic; therefore it may be precipitated by hydrogen sulphide from zinc acetate solutions. This reaction serves to separate zinc from other metals.

Zinc Silicate—$Zn_2SiO_4 + H_2O$—occurs in rhombic crystals as calamine.

CADMIUM.

Cd = 112.1.

Cadmium very often accompanies zinc in its ores. As much as 5 per cent. of this metal is present in the Silesian zinc ores; it was first discovered in these in 1819. Being more volatile than zinc, in obtaining the latter it distils off first, and may be easily separated from the first portions of the distillate. It is a white, tenacious, and rather soft metal, of specific gravity 8.6. It fuses at 315°, and boils at 770°. It does not alter much in the air. Heated, it burns with the separation of a brown smoke of cadmium oxide. It dissolves with difficulty in dilute hydrochloric and sulphuric acids, but readily in nitric. Zinc throws out the metal from solutions of the soluble cadmium salts.

St. Claire Deville found the specific gravity of cadmium vapors (at 1040°) to be 3.9 (air = 1) or 56 (H = 1). Therefore, the molecular weight of cadmium is 112. Since the atomic weight of cadmium (determined from its specific heat) is also 112, it follows that the gas molecule of cadmium consists of but *one* atom. We know that the molecules of other elements in the gaseous state are composed of two or more atoms (O_2,N_2,P_4,S_6). Cadmium, therefore, forms an exception to this rule. This is also true of mercury, and perhaps, too, of other divalent metals, such as zinc. These relations remind us of the behavior of the hydrocarbon residues (radicals); while the divalent or tetravalent groups, *e.g.*, ethylene C_2H_4 and acetylene C_2H_2, exist in free condition, the monovalent groups (as CH_3,CN) cannot appear free, but double themselves, when separated from their compounds.

Of the cadmium compounds may be mentioned:—

Cadmium Hydroxide—$Cd(OH)_2$—is precipitated as a white powder, from the soluble cadmium salts, by the alkalies; it is insoluble in sodium and potassium hydroxides, but dissolves readily in ammonium hydroxide.

Cadmium Oxide—CdO—is prepared by igniting the nitrate. It is a brownish-black powder, consisting of microscopic octahedra.

Cadmous Hydroxide, CdOH, and its *Oxide*, Cd_2O, have been prepared. The first is a grayish white compound, while the second is composed of yellow translucent crystals. It is obtained on heating the hydroxide to a temperature at which sulphuric acid gives off dense white fumes. The hydroxide is a reducing agent, yielding hydrogen with hydrochloric acid and oxides of nitrogen with nitric acid. The oxide conducts itself similarly. These compounds are of interest, as they foreshadow the tendency toward the formation of lower oxides, so strongly shown by mercury (*Am. Chem. Jr.*, 12, 493).

Cadmium Chloride—$CdCl_2$—crystallizes from aqueous solution, with two molecules of H_2O, and may be dried without decomposition. The anhydrous salt melts at 541° and sublimes in scales.

Cadmium Iodide—CdI_2—is obtained by the direct action of iodine upon metallic cadmium in the presence of water. It crystallizes from the latter in hexagonal tables. It is used in photography.

Cadmium Sulphate—$CdSO_4$—crystallizes from water, not like the sulphates of zinc and magnesium, with 7 molecules of H_2O, but with $\frac{8}{3}H_2O$; the crystals effloresce in the air. It, however, forms double salts with the sulphates of the alkali metals, *e. g.*, $CdSO_4.K_2SO_4 + 6H_2O$; these are perfectly analogous to those of zinc and magnesium, and isomorphous with them (p. 318).

Cadmium Sulphide—CdS—occurs native as greenockite, in yellow hexagonal prisms. Hydrogen sulphide precipitates it from cadmium salt solutions as a yellow powder, insoluble in dilute acids. It is employed as a pigment.

Almost all the alloys of cadmium have a low fusion temperature. Freshly prepared cadmium amalgam is a white plastic mass, which soon becomes hard. It is used in filling teeth.

The chemical energy of cadmium is less than that of zinc; this is evident from the fact that the former may be displaced from its salts by the latter. We saw that, with the elements of the groups of potassium and calcium, the chemical energy increases inversely with the increasing atomic weight; cæsium is more energetic than rubidium, barium more than calcium. It is worthy of remark that nearly all of the more electro-negative elements, belonging to the second sub-groups of the seven main groups of the periodic system, exhibit a diminution in chemical energy with rising atomic weight similar to that shown by the members of the magnesium group; copper displaces silver; phosphorus is more energetic than arsenic and antimony; sulphur more energetic than selenium and silver; chlorine sets free or displaces bromine and iodine.

These relations of affinity find full expression in the thermo-chemical phenomena in which are clearly shown the double periodicity of the great periods and the relations of the two sub-groups, Ca, Sr, Ba and Zn, Cd, Hg, to magnesium. The basic character increasing from Mg to Ba corresponds to the increase in heat developed by the formation of their compounds. *e. g.*, the chlorides, hydroxides, and sulphydrates.

$(Mg,Cl_2) = 151.0.$	$(Mg,O,H_2O) = 148.9.$	$(Mg,S,Aq.) =$ ——
$(Ca,Cl_2) = 170.2.$	$(Ca,O,Aq.) = 149.4.$	$(Ca,S,Aq.) = 98.3.$
$(Sr,Cl_2) = 184.5.$	$(Sr,O,Aq.) = 157.7.$	$(Sr,S,Aq.) = 106.6.$
$(Ba,Cl_2) = 194.5.$	$(Ba,O,Aq.) = 158.2.$	$(Ba,S,Aq.) = 107.1.$

That the increase with the hydroxides is so slight is explained probably by the decreasing solubility of the same from Ba to Mg, inasmuch as an evolution of heat (heat of precipitation) corresponds to the difficult solubility. The heat of formation of the carbonates (from metallic oxides and carbon dioxide) must also be introduced here:—

$$(CaO,CO_2) = 42.5 \quad (SrO,CO_2) = 53.2 \quad (BaO,CO_2) = 55.9.$$

These seem to indicate that calcium carbonate is less stable and more easily decomposed than barium carbonate (p. 303).

The series Mg, Zn, Cd, Hg deports itself differently. In this the heat disengagement becomes successively less and corresponds with the diminishing basicity:—

$$\begin{array}{llll} (Mg,Cl_2) = 151.0. & (Mg,O) = 145.0. & (Mg,S) = \text{——} \\ (Zn,Cl_2) = 97.2. & (Zn,O) = 86.4. & (Zn,S) = 41.3. \\ (Cd,Cl_2) = 93.2. & (Cd,O) = 66.4. & (Cd,S) = 33.9. \\ (Hg,Cl_2) = 63.1. & (Hg,O) = 30.6. & (Hg,S) = 16.8. \end{array}$$

Comparing these numbers with the quantity of heat which is disengaged in the formation of aqueous hydrochloric acid ($H,Cl,Aq. = 39.3$), we find explained the behavior of the metals toward this acid. All metals liberating a greater quantity of heat than 39.3 C. in the formation of their chlorides (calculated for 1 equivalent of metal) are in condition to decompose the dilute acid. Most of the metals belong to this class; mercury, copper, silver, gold, lead, thallium, and some others, set free a less amount of heat, and hence are not able to decompose dilute hydrochloric acid (see p. 270)..

The slight quantity of heat developed in the formation of hydrogen sulphide ($S,H_2 = 4.5$) indicates that the same is readily decomposed by all the metals. In the same way, by adding the heat of solution ($S,H_2, Aq. = 9.2$), we can easily ascertain which metals are precipitated by hydrogen sulphide from their chlorides, etc.

If in the thermo-chemical equation,

$$(Me, Cl_2.Aq.) + (S,H_2Aq.) = (Me, S) + 2(H, Cl, Aq.),$$

the sum of the heat developed upon the right side is greater than that upon the left, the reaction will occur (precipitation of metallic sulphides); in the opposite case the sulphide is decomposed by the dilute hydrochloric acid.

The magnitude of the atomic weight of *Mercury* would place the latter in the group of zinc and cadmium. The relationship of these three heavy metals is observed in many similarities of the free elements and of their compounds (p. 325). Occupying a similar position in the three great periods (p. 248) they are distinguished among the heterologous members in a physical point of view by their ready fusibility and volatility, which nearly reach a maximum in them. In the homologous series, Zn, Cd, Hg, these properties, like the specific gravities, increase with rising atomic weight (just as with the metals of the potassium group, p. 277):—

	Zn	Cd	Hg
Atomic weight	65.5	112.1	200.4
Fusing point	412°	315°	—40°
Boiling point	940°	765°	360°
Specific gravity	7.1	8.6	13.6

The gradation in the heat of formation of their compounds (p. 324) clearly indicates that mercury must be arranged in a group with cadmium and zinc.

Like zinc and cadmium, it yields compounds of the form, HgX_2, in which it appears divalent. These derivatives are, in many respects, similar to the corresponding compounds of zinc and cadmium. Thus, mercuric sulphate affords double salts with the alkaline sulphates, which crystallize with six molecules of H_2O ($SO_4Hg.SO_4K_2 + 6H_2O$), and are isomorphous with the double sulphates of the magnesium group (p. 318). The similarity, however, limits itself to few compounds. Since the properties of each group sustain a slight change in virtue of the increasing atomic weight, we are not surprised to observe this to be very evident in the case of Hg (with the high atomic weight 200.4), especially as the middle (transition) member of the third great period is not known (p. 248). Mercury differs essentially from zinc and cadmium* in that, in addition to the compounds of the form $\overset{II}{Hg}X_2$ (mercuric compounds), it is also capable of yielding those of the form $\overset{I}{Hg}X$ (mercurous compounds), in which it seems to be monovalent. Here we meet an instance, frequently observed, in which one and the same metal (as with the most metalloids) is capable of forming compounds of two or more forms, which are to be referred to a different valence of the metal; and it often happens that the derivatives of a metal, appearing in different forms or types, are frequently more essentially distinguished from one another than the compounds of different elements having the same type. Thus, the mercuric compounds (HgX_2) are similar to those of zinc and cadmium, after the same form, while the mercurous compounds ($\overset{I}{Hg}X$) exhibit great resemblance to the cuprous ($\overset{I}{Cu}X$) and silver ($\overset{I}{Ag}X$) compounds, constituted according to a similar type.

It shows that the similarity of the compounds is not only influenced by the nature of the metals, but frequently, to a marked

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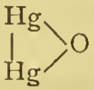
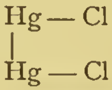
* See p. 255.

degree, by the forms or types according to which they are constituted (p. 333).

As viewed above, mercury in its *ic* compounds is a dyad, in the *ous* a monad. According to the theory of constant valence, the mercury atom in the *ous* compounds is, however, also divalent. We suppose that the molecules of the same are twice as large, and that in them two Hg atoms form a divalent group, as seen from the following :—

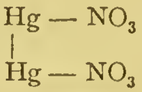


Mercurous oxide.



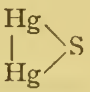
$$\begin{array}{l} Hg - Cl \\ | \\ Hg - Cl \end{array}$$

Chloride.



$$\begin{array}{l} Hg - NO_3 \\ | \\ Hg - NO_3 \end{array}$$

Nitrate.



Sulphide.

This view is, however, not justified, inasmuch as the molecular weight of mercurous chloride corresponds to the formula HgCl (p. 328).

MERCURY.

Hg = 200.4.

Mercury (*Hydrargyrum*) occurs in nature principally as *Cinnabar*, more rarely native in the form of little drops scattered through rocks. Its most important localities are Almaden in Spain, New Almaden in California, Idria in Illyria, Mexico, Peru, China, and Japan.

The metallurgical separation of mercury is very simple. Cinnabar is roasted in reverberatory furnaces, whereby the sulphur burns to dioxide, and the mercury vapors are condensed in large chambers. Or, it is distilled with lime or iron from iron retorts. Commercial mercury usually contains a slight quantity of other metals dissolved in it. For its purification, it is poured in a thin stream into a deep layer of sulphuric or dilute nitric acid, by which the accompanying tin and lead are more easily dissolved than the mercury. The metal is finally distilled out of a small glass retort and pressed through chamois skin.

This is the only metal which is liquid at ordinary temperatures. At 0° its specific gravity equals 13.59; it solidifies at —40°, and crystallizes in regular octahedra; it evaporates somewhat at medium temperatures, and boils at 360°. Its vapors are very poisonous. The specific gravity of the vapor of mercury is 100.2 (H = 1) or 6.91 (air = 1). Therefore, the molecular weight of the metal is 200.4, and as its atomic weight is also 200.4, the molecule, like that of cadmium, is composed of only *one* atom. At ordinary temperatures, mercury is not altered by exposure to the air; near the boiling point, however, it gradually oxidizes to red mercuric oxide. Hydrochloric and cold sulphuric acids do not act upon it; hot sulphuric acid converts it into mercury sulphate, with evolution of sulphur dioxide. Even dilute nitric acid will readily dissolve it. It combines with the halogens and sulphur at ordinary temperatures.

Mercury dissolves almost all metals (not iron) forming amalgams. It unites with potassium and sodium upon gentle warming, with production of heat and light. When the quantity of potassium and sodium exceeds 3 per cent., the alloy is solid and crystalline; by less amount it remains liquid. Tin amalgam is employed for coating mirrors.

Mercury forms two series of compounds, *mercurous* and *mercuric*. The first are analogous to the cuprous, and have the form, HgX. In them mercury appears to be monovalent; we, however, do not know whether their molecules are not to be expressed by the double formula Hg_2X_2 (p. 326). In many respects the *ous* compounds are similar to the cuprous and silver derivatives. The halogen compounds are insoluble, and darken on exposure to light.

In the *ic* derivatives—HgX_2—mercury is divalent, and is very much like zinc and cadmium. The *ic* compounds almost always form, if the substance reacting with the mercury is in excess; when the opposite is the case, mercurous salts result. The *ic* derivatives, by the addition of mercury, pass into the *ous*, *e.g.*, $Hg(NO_3)_2 + Hg = Hg_2(NO_3)_2$. Oxidizing agents convert the *ous* into the *ic* compounds; the latter are, on the other hand, converted by reducing substances into the first.

The heat of formation of some of the mercuric compounds corresponds to the symbols:—

$$(Hg,O) = 30.6 \quad (Hg,Cl_2) = 63.1 \quad (Hg,I_2) = 34.3 \quad (Hg,S) = 16.8.$$

That of the corresponding mercurous salts:—

$$(Hg_2,O) = 42.2 \quad (Hg,Cl) = 41.2 \quad (Hg,I) = 24.2 \quad (Hg_2,S) = —.$$

MERCUROUS COMPOUNDS.

Mercurous Chloride—HgCl or Hg_2Cl_2—calomel, is an amorphous white precipitate, produced by the addition of hydrochloric acid or soluble chlorides to the solution of mercurous salts. It is generally formed by the sublimation of $HgCl_2$ with mercury; or a mixture of $HgSO_4$, mercury and sodium chloride is sublimed:—

$$HgSO_4 + 2NaCl + Hg = Na_2SO_4 + Hg_2Cl_2.$$

It then forms a radiating, crystalline mass (quadratic prisms) of specific gravity 7.2. Calomel is insoluble in water, in alcohol, and dilute acids; it gradually decomposes when exposed to the light, with separation of mercury. When heated, it sublimes without fusing. By the action of strong acids it is converted into mercuric salts and free mercury. When ammonium hydroxide is poured over calomel, it blackens (hence the name calomel, from χαλομελας), and reacts according to the equation :—

$$Hg_2Cl_2 + 2NH_3 = NH_4Cl + NH_2Hg_2Cl.$$

The compound NH_2Hg_2Cl is viewed as ammonium chloride, in which 2H are replaced by Hg_2.

The vapor density of calomel vapors at 440° is 117.6 ($H = 1$), the molecular weight, therefore, 235.2, and corresponds to the formula HgCl (235.2). It appears, however, that its vapors consist of a mixture of mercury and mercuric chloride. Such a mixture must have the same density as HgCl :—

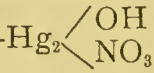
$$\underset{\text{1 vol.}}{HgCl} + \underset{\text{1 vol.}}{HgCl} = \underset{\text{1 vol.}}{Hg} + \underset{\text{1 vol.}}{HgCl_2}.$$

The question, whether the mercurous compounds contain one or two atoms of mercury, whether, for example, the formula Hg_2Cl_2 or HgCl properly belongs to calomel, is, therefore, not decided by the direct determination of its vapor density.

This difficulty has, however, been solved by our better knowledge of the phenomena of dissociation and especially of the tension of dissociation. Pressure obstructs the dissociation of a compound, even though it be heated in the vapor of one of the components, into which it might separate. The determination, therefore, of the vapor density of mercurous chloride in an atmosphere of mercuric chloride has shown it to be 117.6, corresponding to the simple formula HgCl—under this condition a dissociation is impossible (Fileti).

Mercurous Iodide—HgI or Hg_2I_2—is prepared by rubbing together 8 parts of mercury with 5 parts I, or by precipitating mercurous nitrate with potassium iodide. It is a greenish powder, insoluble in water and alcohol. Light changes it to HgI_2 and Hg.

Mercurous Oxide—Hg_2O—is black in color, and is formed by the action of potassium or sodium hydroxide upon mercurous salts. In the light or at 100°, it decomposes into HgO and Hg.

Mercurous Nitrate—$HgNO_3$ or $Hg_2(NO_3)_2$—is produced by allowing somewhat dilute nitric acid to act upon excess of mercury in the cold. It crystallizes with 1 molecule of H_2O in large monoclinic tables. It dissolves readily in water acidulated with nitric acid; pure water decomposes it into the *acid* salt which passes into solution, and the *basic* salt— $Hg_2\begin{cases}OH\\NO_3\end{cases}$, which separates as a yellow powder.

The nitric acid solution of mercurous nitrate oxidizes when exposed to the air, and gradually becomes mercuric nitrate; this may be prevented by adding metallic mercury to the solution, whereby the resultant *ic* salt is again changed to the *ous* state :—

$$Hg(NO_3)_2 + Hg = Hg_2(NO_3)_2.$$

Mercurous Sulphate—$Hg_2(SO_4)$—results when an excess of mercury is heated gently with sulphuric acid ; it separates as a crystalline precipitate, difficultly soluble in water, if sulphuric acid be added to a mercurous nitrate solution. It fuses upon application of heat, and decomposes into SO_2, O_2, and Hg.

Mercurous Sulphide—Hg_2S—is precipitated by potassium hydrosulphide, as a black compound, from the dilute solution of mercurous nitrate. When gently warmed, it decomposes into HgS and mercury.

MERCURIC COMPOUNDS.

Mercuric Chloride—$HgCl_2$—Corrosive sublimate—is produced when mercuric oxide is dissolved in HCl, or metallic mercury in aqua regia. It is obtained on a large scale by the sublimation of a mixture of mercuric sulphate with sodium chloride :—

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4.$$

It crystallizes from water in fine rhombic prisms, and dissolves at medium temperatures in 15 parts, at 100°, in 2 parts water; it is still more soluble in alcohol. Its specific gravity is 5.4. It fuses at 265°, and boils about 293°. Its critical pressure is about 420 Mm. (p. 233). The vapor density is 135.6 (H = 1), corresponding to the molecular formula $HgCl_2$ (= 271.3) :—

$$\underset{\text{1 vol.}}{Hg} + \underset{\text{1 vol.}}{Cl_2} = \underset{\text{1 vol.}}{HgCl_2}.$$

Reducing substances, like SO_2 and $SnCl_2$, change it to insoluble mercurous chloride :—

$$2HgCl_2 + SO_2 + 2H_2O = Hg_2Cl_2 + H_2SO_4 + 2HCl.$$

Stannous chloride first precipitates mercurous chloride: $2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$, which is afterward reduced, by excess of the first, to metallic mercury: $Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4$.

Mercuric chloride is greatly inclined to form double salts with metallic chlorides, *e. g.*, $HgCl_2.KCl + H_2O$. When ammonium hydroxide is added to its solution, a heavy white precipitate, called *white precipitate*, NH_2HgCl, is thrown down. This compound is regarded as a derivative of ammonium chloride, in which two atoms of H are replaced by a divalent mercury atom, and it has been called *Mercur-ammonium Chloride.* It forms the compound

$NH_2HgClNH_4Cl$ with ammonium chloride; the structure of this is expressed by the formula:—

$$Hg\begin{cases}NH_3Cl\\NH_3Cl.\end{cases}$$

Similar mercur-ammonium derivatives are numerous.

Mercuric Iodide—HgI_2—is formed by the direct union of mercury with iodine. When potassium iodide is added to a solution of mercuric chloride, HgI_2 separates as a yellow precipitate, which immediately becomes red. HgI_2 is readily soluble in $HgCl_2$ and KI solutions; it crystallizes from alcohol in bright red quadratic octahedra. Upon warming HgI_2 to 150°, it suddenly becomes yellow, fuses and sublimes in yellow, shining, rhombic needles. On touching these with some solid, they become red, with separation of heat, and are changed into an aggregate of quadratic octahedra. Mercuric iodide is therefore dimorphous.

Mercuric Oxide—HgO—is obtained by the prolonged heating of metallic mercury near the boiling point in the air, or by the ignition of mercurous or mercuric nitrate. It forms a red, crystalline powder, of specific gravity 11.2. When sodium hydroxide is added to a solution of mercuric chloride, mercuric oxide separates as a yellow, amorphous precipitate. Both modifications become black when heated, but change to a yellowish-red on cooling. Mercuric oxide breaks up into mercury and oxygen about 400°.

Mercuric oxide combines directly with ammonia, to form the compound $2HgO.NH_3$, which explodes with violence when heated.

Mercuric Nitrate—$Hg(NO_3)_2$.—It is difficult to obtain this salt pure, because it is inclined to form basic compounds. A solution of it may be made by dissolving mercury or mercuric oxide in an excess of hot nitric acid. On diluting the solution with water the basic salt, $Hg(NO_3)_2.2HgO + H_2O$, separates, and this may be converted into pure mercuric oxide by boiling with water.

Mercuric Sulphate—$HgSO_4$—is produced by digesting mercury or its oxide with an excess of concentrated sulphuric acid. It forms a white, crystalline insoluble mass, which becomes yellow on heating. It yields the hydrate $HgSO_4 + H_2O$ with a little water, but much of the latter decomposes it into sulphuric acid and the yellow insoluble *basic* salt, $HgSO_4.2HgO$ (*Turpetum minerale*, Turpeth mineral).

Mercuric sulphate forms double salts with the alkaline sulphates, *e.g.*, $HgSO_4.K_2SO_4 + 6H_2O$; these are isomorphous with the corresponding double salts of the magnesium group (p. 318).

Mercuric Sulphide—HgS—occurs in nature as *cinnabar*, in radiating crystalline masses, or in hexagonal prisms of red color.

It is obtained by rubbing together mercury and flowers of sulphur with water, or it is produced as a black amorphous mass by the precipitation of a solution of a mercuric salt with hydrogen sulphide. If the black sulphide be heated with exclusion of air it sublimes as a dark red mass of radiating crystalline structure, and is perfectly similar to natural cinnabar. A similar conversion of the black modification into the red is effected by continued heating of the same to 50° with a solution of potassium or ammonium sulphide. The red mercury sulphide thus obtained is employed as *artificial cinnabar* in painting.

The mercury compounds can be readily recognized by the following reactions. On fusion with dry sodium carbonate, mercury escapes, and (if the operation be executed in a small tube) condenses upon the side in metallic drops. Tin, copper and zinc throw out metallic mercury from its solutions. If a pure piece of sheet copper be dipped into the same, mercury is deposited as a gray coating, which on being rubbed acquires a metallic lustre. The mercurous compounds are distinguished from the mercuric by their precipitation by hydrochloric acid.

COPPER, SILVER, AND GOLD.

Considering the magnitude of their atomic weights, copper, silver, and gold, bear the same relation to the alkali group, especially to sodium, as zinc, cadmium, and mercury bear to magnesium :—

Na = 23.06	Mg = 24.38
Cu = 63.3	Zn = 65.5
Ag = 107.938	Cd = 112.1
Au = 197.2	Hg = 200.4.

They occupy an entirely analogous position in the three great periods of the periodic system of the elements (p. 249), and constitute the transition from the elements of group VIII, especially from nickel, palladium, and platinum, to the less basic elements of group II—zinc, cadmium, and mercury :—

Ni = 58.6	Cu = 63.3	Zn = 65.5
Pd = 106	Ag = 107.938	Cd = 112.1
Pt = 194.8	Au = 197.2	Hg = 200.4.

This intermediate position of the three elements about to be discussed is clearly shown in their entire physical deportment. While the elements of group VIII, with the last members, Ni, Pd, and Pt, fuse with difficulty and do not volatilize, Cu, Ag, and Au, in point of fusion and volatility, constitute the transition to the readily fusible and volatile elements, Zn, Cd, and Hg. They take an intermediate position, too, with reference to their coefficients of expansion, their atomic volumes, and other physical properties. It is noteworthy that the ability to conduct heat and electricity attains its maximum in Cu, Ag, and Au. Consult p. 255.

Not only are the properties of the free elements determined by the position of the latter in the periodic system, but those of their derivatives, and especially such as depend upon the valence of the elements, are influenced to a marked degree by the above relation. In consequence of the double periodicity of the great periods, Cu, Ag, and Au attach themselves to group I, and especially to sodium, just as the elements immediately following, Zn, Cd, and Hg, arrange themselves with group II and magnesium. Hence we find Cu, Ag, and Au, like Na, yielding compounds of the form $\overset{I}{Me}X$, in which they appear monovalent. Some of these are isomorphous; thus NaCl, CuCl, and AgCl crystallize in forms of the regular system. Silver sulphate, Ag_2SO_4, is isomorphous with sodium sulphate, SO_4Na_2; and the same is true of other salts of these two metals. Cu and Ag, like the alkalies, afford so-called sub- or quadrant oxides, Na_4O, Cu_4O, Ag_4O.

But we may say that the similarity of Cu, Ag, and Au to Na is confined to these few external properties. Just as the heavy metals, Zn, Cd, and Hg differ in many properties from the light metal magnesium (p. 314), so do the metals Cu, Ag, and Au, possessing a high specific gravity distinguish themselves in a still higher degree from the light metal sodium. They possess all the properties belonging to the heavy metals, which are mainly characterized by the insolubility of the oxides, sulphides, and many salts. This character which separates them from sodium is explained by the fact that they really belong to the three great periods, and are classified with the alkali metals in but few properties. Gold, with the high atomic weight, 197.2, corresponds in this respect to mercury (p. 325), but is very variable.

In the compounds constituted according to the form $\overset{I}{Me}X$, in which Cu, Ag, and Au appear monovalent, they exhibit great similarity in respect to their physical and chemical properties. The chlorides, CuCl, AgCl, and AuCl, are colorless and insoluble in water; soluble, however, in hydrochloric acid, ammonia, the alkaline hyposulphites, etc., and furnish perfectly similar double compounds. While silver only enters compounds of the form $\overset{I}{Ag}X$, copper and gold are capable of yielding another form; copper forms, besides cuprous, $\overset{I}{Cu}X$, also cupric, $\overset{II}{Cu}X_2$, derivatives, in which it appears to be divalent. The latter are much more stable than the former, and embrace the most usual copper salts. Gold, however, besides furnishing *ous*, $\overset{I}{Au}X$, compounds, has *ic* derivatives, $\overset{III}{Au}X_3$, in which it appears trivalent.

While Cu and Au, in their *ous* forms, are analogous to silver (and in less degree, Na), the cupr*ic* derivatives show a great resemblance to the compounds of the metals of the magnesium group, and other metals in their divalent combinations. Thus, the sulphates of zinc, magnesium, cupric oxide (CuO), ferrous oxide (FeO), nickelous oxide (NiO), cobaltous oxide (CoO), and manganous oxide (MnO), are similarly constituted, resemble each other, are isomorphous, and form entirely analogous double salts (p. 318) with the alkaline sulphates. In the same way the carbonates ($\overset{II}{Me}CO_3$), the chlorates and bromates ($\overset{II}{Me}Cl_2O_6 + 6H_2O$) and others, are similarly constituted and isomorphous. In its *ic* derivatives, gold exhibits some similarity to the aluminium compounds ($\overset{III}{Al}X_3$), to those of indium ($\overset{III}{In}X_3$) and other metals, in their trivalent combinations. Here we see, as already observed with mercury (p. 325), that *the similarity of the compounds of the metals is influenced by the similarity of forms or types*, according to which they are composed, *i. e.*, by the valence of the metals. If a metal form several series of compounds of different types, each series is usually more or less similar to the compounds of other metals of like type. In this manner is shown the resemblance of the compounds of the following types :—

Na_2O Sodium oxide.	Ag_2O Silver oxide.	Cu_2O Cuprous oxide.	Au_2O Aurous oxide.	Tl_2O Thallous oxide.
MgO Magnesium oxide.	ZnO Zinc oxide.	CuO Cupric oxide.	FeO Ferrous oxide.	HgO Mercuric oxide.
Al_2O_3 Aluminium oxide.	Fe_2O_3 Ferric oxide.	Au_2O_3 Auric oxide.	Tl_2O_3 Thallic oxide.	

The character of their derivatives varying with the degree of combination or valence, becomes quite marked with chromium, manganese and iron, as we shall later see. The heavy metals also exhibit a strong, positive basic character in their monovalent combinations. Thus silver oxide (Ag_2O) and thallous oxide (Tl_2O) are strong bases, forming neutral reacting salts with acids, and even cuprous and aurous oxides are more strongly basic than their higher forms of oxidation. The metalloidal character of the metals, and the acid nature of their oxides begin to appear in their trivalent combinations. Thus in the hydroxyl derivatives of aluminium, indium, and gold, $Al(OH)_3$, $In(OH)_3$, $Au(OH)_3$, hydrogen may be replaced by the alkalies just as in boric acid, $B(OH)_3$. Their higher forms of oxidation show, like those of the metalloids, a pronounced acid-like character (as PbO_2, PtO_2, CrO_3, FeO_3) which is only lessened by a high atomic weight of the metal (as in PbO_2 and PtO_2). The character of the compound is influenced in a less, if not an unimportant degree, by the position of the elements in the periodic system. Hence the properties of the metallic compounds are not only influenced by the nature of the metals, but to a high degree by the combination forms. These forms of the elements, and particularly those of the metals, are regulated, however, if not entirely, yet to a considerable degree, by the periodic system, as previously observed (see p. 252).

This connection of Cu, Ag, and Au in an analogous group, expresses itself, too, in the heat resulting from the formation of their compounds of the form MeX:—

$(Na, Cl) = 97.6$ $(Na_2, O) = 100.2$ $(Na_2, S)\ 88.0.$
$(Cu, Cl) = 32.8$ $(Cu_2, O) = 40.8$ $(Cu_2, S)\ 20.2.$
$(Ag, Cl) = 29.3$ $(Ag_2, O) = 5.9$ $(Ag_2, S)\ 5.3.$
$(Au, Cl) = 5.8$ $(Au_2, O) =$ — (Au_2, S) —.

Consequently relations occur here perfectly similar to those of the elements of the zinc group (p. 323), and perfectly analogous conclusions may be deduced from them with respect to the affinity relations. Thus, for example, copper is able to decompose concentrated but not dilute hydrochloric acid. The heat of formation of some cupric compounds equals:—

$(Cu, O) = 37.1$ $(Cu, Cl_2) = 51.6$ $(Cu, Cl_2, Aq.) = 62.7$
$(Cu, S, O_4) = 182.$

COPPER.

$Cu = 63.3.$

Native copper is found in large quantities in America, China, Japan, also in Sweden and in the Urals. It frequently occurs crystallized in cubes and octahedra. The most important and most widely distributed of its ores are: cuprite (Cu_2O), malachite and azurite (basic carbonates), chalcocite (Cu_2S), and especially chalcopyrite or speckled copper ore ($CuFeS_2$).

Metallurgy of Copper.—The extraction of copper from its oxygen ores is very simple: metallic copper is melted out when the ores are ignited along with charcoal. The sulphur ores are more difficult to work. The divided material is first roasted in the air, by which means copper sulphide is partially converted into oxide. The mass is afterward ignited with sand, silica fluxes, and carbon, when iron sulphide is converted into oxide and passes into the slag. By several repetitions of this process we get the so-called *copper stone*—a mixture of cupric sulphide with oxide. This is repeatedly roasted and heated, and metallic copper obtained by the action of the cupric oxide upon the sulphide :—

$$2CuO + CuS = 3Cu + SO_2.$$

The copper obtained in this way is fused again with charcoal, to free it from the oxide.

To obtain chemically pure copper, the pure oxide is heated in a stream of hydrogen, or the solution of copper sulphate is decomposed by electrolysis.

Metallic copper possesses a characteristic red color, and transmits a green light in thin leaflets. It is rather soft and ductile, and possesses a specific gravity 8.9. It fuses about 1054°, and vaporizes in the oxy-hydrogen flame. It remains unaltered in dry air; in moist, it is gradually coated with a green layer of copper carbonate. When heated, it oxidizes to black cupric oxide.

Copper is not changed by dilute hydrochloric or sulphuric acids; if it be moistened with these, and exposed to the air, it absorbs oxygen, and gradually dissolves. It is similarly dissolved by ammonium hydroxide. Concentrated sulphuric acid converts it into copper sulphate, with evolution of sulphur dioxide. It dissolves in dilute nitric acid in the cold, with evolution of nitric oxide. Zinc, iron and also phosphorus precipitate metallic copper from the aqueous solutions of its salts.

Copper forms two series of compounds, known as cupr*ous* and cupr*ic*. In the *ic* compounds, copper is divalent :—

$$CuO \quad CuCl_2 \quad Cu(OH)_2 \quad SO_4Cu.$$

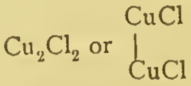
These are more stable than the *ous* derivatives; the ordinary copper salts belong to them. In many respects they resemble the compounds of other dyad metals, especially those of the magnesium group, and *ous* compounds of iron (FeO), manganese (MnO), cobalt and nickel (see p. 333).

The cuprous compounds are, on the other hand, very unstable, absorb oxygen from the air, and pass into cupric derivatives. They show some similarity to the mercurous derivatives (p. 327), and possess an analogous composition :—

$$CuCl \quad CuI \quad Cu_2O \quad Cu_2S.$$

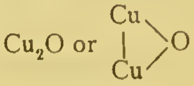
Oxygen salts of cuprous oxide are not known.

From the formulas given above, copper, like silver, is monovalent in its *ous* compounds. It is, however, questionable, whether these formulas express the real molecular values. It is ordinarily assumed that the cuprous derivatives, like those of mercury in its *ous* state (p. 328), correspond to the doubled formulas, and that the copper atom is divalent, and forms a divalent group composed of two copper atoms, as may be seen from the following formulas:—



$$Cu_2Cl_2 \text{ or } \begin{matrix} CuCl \\ | \\ CuCl \end{matrix}$$

Cuprous chloride.



$$Cu_2O \text{ or } \begin{matrix} Cu \\ | \\ Cu \end{matrix}\!\!>\!O$$

Cuprous oxide.

The vapor density of cuprous chloride corresponds to the formula Cu_2Cl_2 (compare p. 342), and, therefore, rather favors the above opinion.

CUPROUS COMPOUNDS.

Cuprous Oxide—Cu_2O—occurs as cuprite crystallized in regular octahedra. It is obtained artificially by boiling a solution of copper sulphate and grape sugar with potassium hydroxide, when it separates as a crystalline, bright-red powder. It does not change in the air, and is readily soluble in ammonium hydroxide. The solution absorbs oxygen, and while forming cupric oxide acquires a blue color. By the action of sulphuric and other oxygen acids, it forms cupric salts, the half of the copper separating as metal:—

$$Cu_2O + SO_4H_2 = CuSO_4 + Cu + H_2O.$$

The hydroxide, $Cu_2(OH)_2$, is precipitated by the alkalies as a yellow powder from hydrochloric acid solutions of Cu_2Cl_2. It oxidizes in the air to cupric hydroxide.

Cuprous Chloride—CuCl or Cu_2Cl_2—is produced by the combustion of metallic copper in chlorine gas (together with $CuCl_2$), upon conducting HCl over copper at a low, red heat, by boiling the solution of cupric chloride with copper ($CuCl_2 + Cu = Cu_2Cl_2$), and by the action of many reducing substances upon cupric chloride. It is most conveniently made by passing sulphur dioxide through a concentrated solution of copper sulphate and sodium chloride, when it separates as a white, shining powder, consisting of small tetrahedra. It fuses at 430°, and distils about 1000°; its vapor density corresponds to the formula Cu_2Cl_2. In the air, it rapidly becomes green, owing to oxygen absorption, and the formation of basic cupric chloride, $Cu\begin{matrix}\diagup Cl \\ \diagdown OH\end{matrix}$. Cuprous chloride is readily soluble in concentrated hydrochloric acid and in ammonium hydroxide; both solutions possess the characteristic property of absorbing carbon monoxide.

Cuprous Iodide—CuI or Cu_2I_2—is precipitated from soluble cupric salts by potassium iodide:—

$$CuSO_4 + 2KI = CuI + K_2SO_4 + I.$$

By extracting the co-precipitated iodine by means of ether it is obtained as a gray powder, insoluble in acids.

Cuprous Sulphide—Cu_2S—occurs as chalcocite crystallized in rhombic forms. It is produced by burning copper in vapor of sulphur, and by heating cupric sulphide in a current of hydrogen; after fusion it solidifies in crystals of the regular system. Combined with silver sulphide it constitutes the mineral stromeyerite, $\left.\begin{matrix}Cu\\Ag\end{matrix}\right\}S$ or $Cu_2S.Ag_2S$, isomorphous with chalcocite.

Copper Hydride—CuH or Cu_2H_2—belongs to the derivatives of monovalent copper. If a solution of copper sulphate be digested with hypophosphorous acid, the hydride separates as a yellow amorphous precipitate which soon acquires a brown color. At 60° it decomposes into copper and hydrogen.

With hydrochloric acid it forms cuprous chloride:—

$$CuH + HCl = CuCl + H_2.$$

Copper suboxide, Cu_4O, or quadrantoxide, corresponds to potassium suboxide. On adding an alkaline stannous chloride solution to one of copper sulphate there separates, at first, cupric hydroxide, which is further reduced to cuprous hydroxide, and then to suboxide. The latter is an olive-green powder, which oxidizes readily and is decomposed by H_2SO_4 into $CuSO_4$ and 3Cu.

CUPRIC COMPOUNDS.

The cupric salts, when hydrous, are generally colored blue or green; they are colorless in the anhydrous condition.

Cupric Hydroxide—$Cu(OH)_2$—separates as a voluminous bluish precipitate when sodium or potassium hydroxide is added to soluble copper salts. When heated, even under water, it loses water, and is changed to black cupric oxide.

Cupric Oxide—CuO—is usually obtained by the ignition of copper turnings in the air, or by heating cupric nitrate. It forms a black amorphous powder, which, at higher temperatures, settles together and acquires a metallic lustre. By heating with organic substances their carbon is converted into carbon dioxide, and the hydrogen into water, the cupric salt being reduced to metal; upon this rests the application of cupric oxide in the analysis of such compounds.

Copper oxide and hydroxide dissolve in ammonium hydroxide with dark blue color. The solution possesses the power of dissolving wood fibre (cotton-wool, linen, filter-paper, etc.)—*Schweizer's reagent*.

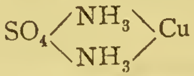
Cupric Chloride—$CuCl_2$—is formed by the solution of cupric oxide or carbonate in hydrochloric acid. It crystallizes from aqueous solution, with 2 molecules of water, in bright green rhombic needles, and is readily soluble in water and alcohol. When heated, it parts with its water, becoming anhydrous chloride, which at a red heat is decomposed into chlorine and cuprous chloride. It yields beautifully crystallized double salts with potassium and ammonium chlorides. Cupric bromide is like the chloride; the iodide is not known, since in its formation it at once breaks up into cuprous iodide and iodine.

Copper Sulphate—$CuSO_4 + 5H_2O$—cupric sulphate, copper vitriol—may be obtained by the solution of copper in concentrated sulphuric acid. It is produced on a large scale by roasting chalcocite. It forms large blue crystals of the triclinic system, which effloresce somewhat upon exposure. At 100° the salt loses 4 molecules of water; the fifth separates above 200°. The anhydrous sulphate is colorless, absorbs water very energetically, and returns to the blue hydrous compound.

Although copper sulphate only crystallizes with 5 molecules of H_2O, it is capable, like the sulphates of the magnesium group, of forming double salts with potassium and ammonium sulphates, which crystallize with $6H_2O$, and are isomorphous with the double salts of the metals of the magnesium group.

Copper sulphate is employed in electro-plating. When its solution is decomposed by the galvanic current copper separates at the negative pole, and deposits in a regular layer upon the conducting objects connected with the electrode.

Ammonium hydroxide added to a copper sulphate solution in sufficient quantity to dissolve the cupric hydroxide produced at first, changes the color of the liquid to a dark blue. From this solution alcohol precipitates a dark-blue crystalline mass with the composition $CuSO_4.4NH_3 + H_2O$. Heated to 150° this compound loses water and 2 molecules of NH_3, and becomes $CuSO_4.2NH_3$. It is supposed that these compounds are ammonium salts in which a part of the hydrogen is replaced by copper; they have been designated *cuprammonium compounds, e. g.*:—

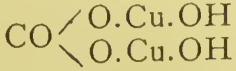


Cuprammonium sulphate.

The other soluble copper salts afford similar compounds with ammonium hydroxide.

Cupric Nitrate—$Cu(NO_3)_2$—crystallizes with three or six molecules of water, has a dark-blue color and is readily soluble in water and alcohol. Heat converts it into cupric oxide.

Copper Carbonates.—The neutral salt ($CuCO_3$) is not known.

When sodium carbonate is added to a warm solution of a copper salt the basic carbonate, $CuCO_3.Cu(OH)_2$, or  $\mathrm{CO}\left\langle\begin{array}{l}\mathrm{O.Cu.OH}\\ \mathrm{O.Cu.OH}\end{array}\right.$' separates as a green precipitate. It occurs in nature as *malachite*, which is especially abundant in Siberia. Another basic salt—$2CO_3Cu.Cu(OH)_2$—is the beautiful blue *azurite*.

Copper Arsenite—$(AsO_3)_2Cu_3$—separates as a beautiful bright green precipitate, upon the addition of sodium arsenite to a copper solution. It was formerly employed as a pigment, under the name of *Scheele's green*, but at present, owing to its poisonous character, it has been replaced by other green colors (Guignet's green and aniline green).

Cupric Sulphide—CuS—is a black compound, precipitated from copper solutions by hydrogen sulphide. It is insoluble in dilute acids. When moist, it slowly oxidizes in the air to cupric sulphate. Heated in a stream of hydrogen, it forms cuprous sulphide, Cu_2S.

Alloys of Copper.—Pure copper is very ductile, and may be readily rolled, and drawn out into a fine wire. It cannot be well poured into moulds, because it contracts unequally upon cooling and does not fill out the moulds. For such purposes, alloys of copper are employed, which, in addition, possess other technically valuable properties. The most important copper alloys are :—

Brass, consisting of two or three parts copper and one part zinc. It has a yellow color, and is considerably harder than pure copper. Ordinarily, one to two per cent. of lead are added to the brass, which facilitates its working upon the turning-lathe. *Tombac* contains 15 per cent. zinc, and has a gold-like color. The alloy of 1 part zinc and 5.5 parts copper answers for the manufacture of spurious gold leaf. The alloys of copper with tin are called *bronzes*. Most of the modern bronzes also contain zinc and lead; those from Japan, gold and silver. The *cannon bronze* contains 90 per cent. copper and 10 per cent. tin; bell metal has 20–25 per cent. of tin.

Argentan is an alloy of copper, zinc, and nickel (see latter). The German copper coins consist of 95 per cent. Cu, 4 per cent. Sn, and 1 per cent. Zn.

Of the more recently introduced alloys of copper we may mention :—

Phosphorus Bronze. This consists of 90 parts copper, 9 parts tin and 0.5–0.8 parts phosphorus. By the latter ingredient the bronze is increased in hardness, and its solidity and resistance to oxidation are also increased. It is employed in making machinery.

Silicon bronze, containing silicon instead of phosphorus, is characterized by great firmness and conductivity. It is used for telephone wires.

Manganese bronze contains 70 per cent. copper and 30 per cent. manganese (it is the cupro-manganese of Létrange), and may be melted with copper and copper alloys, imparting to these solidity and great hardness. See p. 351 for aluminium bronze.

Recognition of Copper Compounds.—Most copper compounds containing water have a blue or green color. With the exception of copper sulphide they all dissolve in ammonium hydroxide, with a blue color. When a piece of pure iron is introduced into a copper solution, it becomes covered with a red layer of metallic copper. Volatile copper compounds tinge the flame blue or green. The spectrum of such a flame is characterized by several blue and green lines.

SILVER.

Ag = 107.938.

Silver occurs native. Its most important ores are Ag_2S and various compounds with sulphur, arsenic, antimony, copper and other metals. Of rarer occurrence are combinations with chlorine (hornsilver, AgCl), bromine and iodine. Slight quantities of silver sulphide are present in almost every galenite (PbS). The principal localities for silver ores are America (Chili, Mexico, California), Saxony (Freiberg), Hungary, the Altai and Nertschinsk.

Metallurgy of Silver.—The separation of the metal from its ores is rather complicated and variously effected; its elaborate description belongs to the province of metallurgy. At present, the ores containing silver and copper are, in Saxony and the Hartz, roasted in a divided state and fused with slags rich in silicic acid. In this way, as with copper, there is obtained a copper stone consisting of iron, copper and silver sulphides. This is then oxidized in a furnace; from the resulting mixture of ferric and cupric oxides and silver sulphate (SO_4Ag_2), the latter is extracted by water. The silver is precipitated from this aqueous solution by copper.

Formerly, in Saxony, the separation of the silver was executed according to the so-called amalgamation process. According to this the mixture of sulphides is roasted with sodium chloride, whereby silver chloride is produced. The divided material is then mixed with iron scraps and water in rotating vessels. The iron causes the precipitation of the metallic silver from its chloride :—

$$2AgCl + Fe = FeCl_2 + 2Ag.$$

To free the metal from various impurities it is dissolved in mercury and the liquid amalgam ignited; mercury distils off and silver remains. Owing to scarcity of combustible material, the conversion of silver ores into silver chloride is executed, in Mexico and Peru, by mixing the ores with sodium chloride and copper sulphate in the presence of water. In this way cuprous chloride is produced, which is transposed, with silver sulphide, into silver chloride and cuprous sulphide :—

$$2CuCl + Ag_2S = Cu_2S + 2AgCl.$$

To get silver from galenite, proceed as follows: First, metallic lead is obtained. In this way all the silver in the ore passes into the lead and may be obtained with profit from the latter, even if it does not constitute more than $\frac{1}{100}$ per cent. of it. To this end, the metallic lead is fused and allowed to cool slowly; pure lead first crystallizes out, which can be removed by sieves, while a readily fusible alloy of lead with more silver remains behind. This method of Pattison's is repeated until the residual liquid lead contains 1 per cent. of silver. The lead, rich in silver, is subjected to cupellation; it is fused in a reverberatory furnace with air access. The bottom of the oven consists of some porous substance. In this process the lead is changed to readily fusible oxide, which partly flows out of side openings from the hearth, or is, in part, absorbed by the porous bed; the unoxidized silver remains in the cupel in metallic condition.

The ordinarily occurring silver (work silver) is not pure, but invariably contains copper and traces of other metals in greater or less quantity. To prepare chemically pure metal, the work silver is dissolved in nitric acid, and from the solution of nitrates thus obtained, hydrochloric acid precipitates the silver as chloride:—

$$AgNO_3 + HCl = AgCl + HNO_3.$$

The latter is reduced by various methods; either by fusion with sodium carbonate, or by the action of zinc or iron in the presence of water:—

$$2AgCl + Zn = ZnCl_2 + 2Ag.$$

Silver is a pure white, brilliant metal, of specific gravity 10.5. It is tolerably soft and very ductile, and can be drawn out to a fine wire. It crystallizes in regular octahedra. It fuses at 954°, and is converted into a greenish vapor in the oxy-hydrogen flame. Silver is not oxidized by oxygen; by the action of ozone it is covered with a very thin layer of silver peroxide. When in molten condition, silver absorbs 22 volumes of oxygen without combining chemically with it; the absorbed gas escapes again when the metal cools.

Silver is capable of existing in three allotropic forms, which have properties greatly different from those of ordinary silver. The first form is soluble in water and has a blue color. The second variety is insoluble, and somewhat resembles the first form. The third closely resembles gold in color and lustre. These allotropic varieties of silver are broadly distinguished from normal silver by color. They very likely are more active conditions of silver, common silver being a polymerized variety (*Am. Jr. Science*, 37, 476).

Silver unites directly with the halogens; by the action of hydrochloric acid it becomes coated with an insoluble layer of silver chloride. Boiled with strong sulphuric acid, it dissolves to sulphate:—

$$2Ag + 2H_2SO_4 = Ag_2SO_4 + SO_2 + 2H_2O.$$

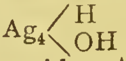
The best solvent of silver is nitric acid, which even in a dilute state and unaided by heat, converts it into nitrate.

As silver is rather soft, it is usually employed in the arts alloyed with copper, whereby it acquires a greater hardness. Most silver coins consist of 90 per cent. silver and 10 per cent. copper; the English shillings contain 92.5 per cent. silver.

Oxygen forms three compounds with silver, but only the oxide affords corresponding salts.

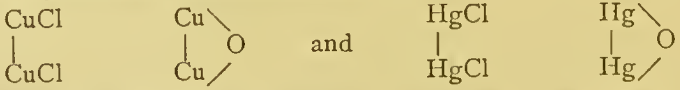
Silver Oxide—Ag_2O—is thrown out of a silver nitrate solution by sodium or potassium hydroxide as a dark-brown, amorphous precipitate. It is somewhat soluble in water, and blues red litmus paper. In this, and in the neutral reaction of the nitrate, the strong, basic, alkaline nature of silver and its oxide exhibits itself; the soluble salts of nearly all of the other heavy metals show an acid reaction. When heated to 250°, the oxide decomposes into metal and oxygen; at 100° it is reduced by hydrogen. The hydrated oxide is not known; the moist oxide reacts, however, very much like the hydroxides.

On dissolving precipitated silver oxide in ammonium hydroxide, black crystals ($Ag_2O.2NH_3$) separate when the solution evaporates, and when dry these explode upon the slightest disturbance. (Fulminating silver.)

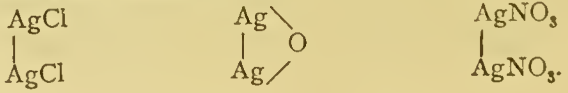
Silver Suboxide—Ag_4O—corresponding to potassium suboxide, is produced by heating silver citrate in a current of hydrogen, and is a black, very unstable powder, which decomposes readily into silver oxide and silver. v. d. Pfordten has recently shown that this product is really a silver hydroxide and assigns the formula  $Ag_4\begin{cases}H\\OH\end{cases}$ to it.

Silver Peroxide—AgO or Ag_2O_2—is formed by passing ozone over silver or its oxide, or by the decomposition of the nitrate by the electric current. It consists of black, shining octahedra, and at 100° decomposes into Ag_2O and oxygen.

The salt-like compounds of silver correspond to the oxide Ag_2O, and are all constituted according to the form AgX, hence are termed argentic. They are analogous to the cuprous and mercurous derivatives, and show a great resemblance to the former in physical and chemical qualities. It would, therefore, be more correct to designate them argent*ous*. Compounds of the divalent form AgX_2, are not known for silver. If, however, the mercurous and cuprous compounds are expressed by double formulas (p. 336):—



which view is supported by their chemical deportment, those of silver might be represented by analogous formulas:—



Then the silver atom would be divalent and a complete parallelism would be established with copper. The chemical formulas of solid bodies do not generally designate their true molecular values as in the case of gases, but only their simplest atomic composition. It is very probable that even the simplest chemical compounds, *e.g.*, KCl and AgCl, consist in their solid condition (as crystal molecules, p. 107) of complex molecules corresponding to the formulas $(KCl)_n$, $(AgCl)_m$. An argument supporting this view is afforded by the existence of different modifications of chloride and bromide of silver; these differ from each other in their external properties, and in their different susceptibilities to light. The doubling of formulas, as shown above with Cu_2Cl_2, Hg_2Cl_2 etc., is mainly due to the tendency to deduce all the compounds of an element from a constant value, according to the doctrine of constant valence. This is, however, impossible (p. 175). According to present notions of valence, and as it is presented in the periodic system, compounds (MeCl, $MeCl_2$, $MeCl_3$, etc.) are constituted according to definite forms or types that may materially determine their properties (p. 333). So far as the similarity of metallic compounds is concerned, it is of secondary importance whether the quantities corresponding to the simple formulas, in the solid or gaseous state, do unite to larger, complex molecules (compare HgCl, Cu_2Cl_2 — BCl_3, $Al(CH_3)_3$ and Al_2Cl_6, $GaCl_3$ and Ga_2Cl_6 — $SnCl_2$, Sn_2Cl_4, $PbCl_2$, etc.). In case of the sesquioxides M_2O_3 it is also immaterial whether they are derived from supposed trivalent elements (as Al_2O_3, Ga_2O_3, In_2O_3), or from those that are tetravalent (as Fe_2O_3, Cr_2O_3, Mn_2O_3). The same may be remarked of the metallic compounds $Me_3O_4 = (MeOO)_2.Me$ (see Spinels).

The use of simple or of double formulas for the metallic compounds is therefore of no special importance.

Silver Chloride—AgCl—exists in nature as hornsilver. When hydrochloric acid is added to solutions of silver salts, a white, curdy precipitate separates; the same fuses at 451° to a yellow liquid, which solidifies to a horn-like mass. The chloride is insoluble in dilute acids; it dissolves somewhat in concentrated hydrochloric acid and in sodium chloride, readily in ammonium hydroxide, potassium cyanide, and sodium hyposulphite. It crystallizes from ammoniacal solutions in large, regular octahedra. Dry silver chloride absorbs 10 per cent. of ammonia gas, forming a white compound—$2AgCl.3NH_3$—with it, which at 38° gives up its ammonia.

Silver Bromide—AgBr—is precipitated from silver salts by hydrobromic acid or soluble bromides. It has a bright yellow color, and dissolves with more difficulty than the chloride in ammonium hydroxide; in other respects it is perfectly similar to the latter. Heated in chlorine gas it is converted into chloride.

Silver Iodide—AgI—is distinguished from the chloride and bromide by its yellow color, and its insolubility in ammonia. Fused silver iodide at first solidifies in isometric crystals, which gradually change to hexagonal forms, but when the latter are heated to 146°, they suddenly revert to the isometric forms. It dissolves readily in hydriodic acid, to AgI.HI, which, upon evaporation of the solution, separates in shining scales. Heated in chlorine or bromine gas, it is converted into chloride or bromide; conversely, chloride and bromide of silver are converted into silver iodide by the action of hydriodic acid.

These opposite reactions are explained by the principle of the greatest evolution of heat. Chlorine and bromine expel iodine from all iodides because the heat of formation of the latter is less than that of the bromides and chlorides (p. 271). Again, hydriodic acid (gaseous or in aqueous solution) converts silver chloride into the iodide according to the equation:—

$$AgCl + HI = AgI + HCl,$$

because the heat modulus of the reaction is positive (for gaseous HI and HCl + 12.5 C., for the solution + 10.6 C. See the Table at close of book).

Sunlight, and also other chemically active rays (magnesium light, phosphorus light) color silver chloride, bromide, and iodide, at first violet, then dark black, whereby they are probably converted into compounds of the form Ag_2X. In such an altered condition they are capable of fixing finely divided silver; on this depends their application in photography.

In photographic work a *negative* is first prepared. A glass plate is covered with collodion (a solution of pyroxylin in an ethereal solution of alcohol) holding in solution halogen salts of calcium or cadmium. After the evaporation of the ether the glass plate is covered by a dry collodion layer containing the haloid salts. The plate is now immersed in a solution of silver nitrate, whereby haloid salts of silver are precipitated upon the surface. The plate thus prepared is exposed to light in the camera obscura, and, after the action, dipped into a solution of pyrogallic acid or ferrous sulphate. These reducing substances separate metallic silver in a finely divided state, which is precipitated upon the places where the light has acted. The plate is now introduced into a solution of potassium cyanide, which dissolves the silver salts not affected by the light, while the metallic unaltered silver remains. The negative thus formed is covered at the places upon which the light shone, by a dark layer of silver, while the places corresponding to shadows of the received image are transparent. The copying of the glass negative on paper is executed in a similar manner.

Silver Cyanide—AgCN—is precipitated from silver solutions by potassium cyanide or aqueous hydrocyanic acid, as a white, curdy mass, not affected by light. It dissolves readily in ammonium hydroxide and potassium cyanide, forming with the latter the crystalline compound AgCN.KCN. The solution in potassium cyanide is employed in the *electro silver-plating* of metals.

Silver Nitrate—$AgNO_3$—is obtained by dissolving pure silver in somewhat dilute nitric acid, and crystallizes from its aqueous solution in large rhombic tables, isomorphous with potassium saltpetre. At ordinary temperatures it is soluble in one-half part water or in four parts alcohol, the solution having neutral reaction. In this respect it differs from the salts of almost all metals, which react acid (p. 333). It fuses at 218°, and solidifies to a crystalline mass. When perfectly pure it is not affected by light, but it usually turns black in sunlight with separation of metallic silver. Organic substances also reduce it to metal. Silver nitrate is employed in the cauterization of wounds (Lunar caustic).

By dissolving work silver in nitric acid a mixture of silver and copper nitrates is obtained. To separate the silver salt from such a mixture it is heated to redness, the copper thus converted into oxide and the unaltered silver nitrate extracted with water.

Silver Nitrite—$AgNO_2$—is precipitated from concentrated silver nitrate solutions by potassium nitrite. It crystallizes in needles, dissolves with difficulty in water, and decomposes above 90°.

Silver Sulphate—Ag_2SO_4—is obtained by the solution of silver in hot sulphuric acid, and crystallizes in small rhombic prisms which are difficultly soluble in water. It is isomorphous with anhydrous sodium sulphate.

Silver Sulphite—Ag_2SO_3—is precipitated as a white, curdy mass, if sulphurous acid be added to the solution of the nitrate. It blackens in the light and decomposes at 100°.

Silver Sulphide—Ag_2S—occurs in regular octahedra, as argentite. Hydrogen sulphide precipitates it as a black amorphous sulphide from silver solutions. By careful ignition in the air it is oxidized to silver sulphate. It is insoluble in water and ammonium hydroxide and dissolves with difficulty in nitric acid.

Silvering.—When silver contains more than 15 per cent. copper it has a yellowish color. To impart a pure white color to objects made of such silver they are heated to redness with access of air. The copper is thus superficially oxidized, and may be removed by dilute sulphuric acid. The surface of pure silver is then polished.

The silvering of metals and alloys (German silver, argentan) is executed in a dry or wet way. In the first, the objects to be silvered are coated with liquid silver amalgam, with a brush, and then heated in an oven; the mercury is volatilized, and the silver surface then polished.

At present, the galvanic process has almost completely superseded the other processes. It depends on the electrolysis of the solution of the double cyanide of silver and potassium, whereby the silver is thrown out upon the electro-negative pole and deposits upon the metallic surface in connection with that electrode.

To silver glass, cover it with a mixture of an ammoniacal silver solution, with reducing organic substances like aldehyde, lactic, and tartaric acids. Under definite conditions, the reduced silver deposits upon the glass as a regular metallic mirror.

Recognition of Silver Compounds.—Hydrochloric acid throws down a white, curdy precipitate of silver chloride, which dissolves readily in ammonium hydroxide. Zinc, iron, copper, and mercury throw out metallic silver from solutions of silver salts, and from insoluble compounds, like the chloride.

GOLD.

$Au = 197.2$

Gold (*aurum*) usually occurs in the native state, and is found disseminated in veins in some of the oldest rocks. Gold sands are formed by the breaking and disintegration of these. It is found, in slight quantity, in the sand of almost every river. Combined with tellurium it forms sylvanite, found in Transylvania and California. It is present in minute quantity in the most varieties of pyrites and in many lead ores. For the separation of the gold grains the sand or pulverized rocks are washed with running water, which removes the lighter particles and leaves the specifically heavier gold.

Native gold almost invariably contains silver, copper, and various other metallic admixtures. To remove these, the gold is boiled with nitric or concentrated sulphuric acid. The removal of the silver by the latter acid is only complete if that metal predominates; in the reverse case a portion of it will remain with the gold. Therefore, to separate pure gold from alloys poor in silver they must first be fused with about three-fourths their weight of the latter metal. Gold may be separated from copper and lead by cupellation (p. 341).

Pure gold is rather soft (almost like lead) and has a specific gravity 19.32. It is the most ductile of all metals, and may be drawn out into extremely fine wire and beaten into thin leaves, which transmit green light. About 1035° it melts to a greenish liquid. It is not altered by oxygen, even upon ignition; acids do not attack it. It is only in a mixture of nitric and hydrochloric acids (aqua regia), which yields free chlorine, that it dissolves to gold chloride, $AuCl_3$. Free chlorine produces the same. Most metals, and many reducing agents (ferrous sulphate, oxalic acid) precipitate gold from its solution as a dark-brown powder.

As gold is very soft it wears away rapidly, and is, therefore, in its practical applications, usually alloyed with silver or copper, which have greater hardness. The alloys with copper have a reddish color, those with silver are paler than pure gold. The German, French, and American gold coins contain 90 per cent. gold and 10 per cent. copper. A 14-karat gold is generally employed for ornamental objects; this contains about 58.3 per cent. pure gold (24 karats representing pure gold).

Gold, according to its atomic weight, belongs to the group of copper and silver; and, upon the other hand, forms the transition from platinum to mercury. Its character is determined to a high degree by these double relations (p. 331). Like the other elements of high atomic weight, mercury, thallium, lead, and bismuth, belonging to the same series of the periodic system, it varies considerably in character from its lower analogues.

Gold, like silver and copper, yields compounds of the form AuX—aurous, analogous to the cuprous and argentous. Besides, it has those of the form AuX_3, auric derivatives, in which it is trivalent. These show the typical character of the trivalent combination form, which expresses itself in the acidity of the hydroxides (p. 333); auric hydroxide, $Au(OH)_3$, unites almost solely with bases. On the other hand, they show many similarities to the highest combination forms of the metals with high atomic weight: platinum (PtX_4), mercury (HgX_2), thallium (TlX_3), and lead (PbX_4) (p. 360).

AUROUS COMPOUNDS.

Aurous Chloride—AuCl—is produced by heating auric chloride, $AuCl_3$, to 180°, and forms a white powder insoluble in water. When ignited, it decomposes into gold and chlorine; boiled with water it decomposes into the trichloride and gold.

Aurous Iodide—AuI—separates as a yellow powder, if potassium iodide be added to a solution of auric chloride:—

$$AuCl_3 + 3KI = AuI + I_2 + 3KCl.$$

When heated it breaks up into gold and iodine.

When auric oxide or sulphide is dissolved in potassium cyanide, large colorless prisms of the double cyanide, AuCN.KCN, crystallize out upon evaporation. The galvanic current and many metals precipitate gold from this compound; hence it serves for electrolytic gilding, which, at present, has almost entirely superseded the gilding in the dry way (see p. 345).

Aurous Oxide—Au_2O—is formed by the action of potassium hydroxide upon aurous chloride. It is a dark violet powder which at 250° decomposes into gold and oxygen. It is changed to $AuCl_3$ and gold by the action of hydrochloric acid.

Only a few double salts of the oxygen derivatives of monovalent gold are known.

AURIC COMPOUNDS.

Auric Chloride—$AuCl_3$—results by the solution of gold in aqua regia, and by the action of chlorine upon the metal. When the solution is evaporated the chloride is obtained as a reddish-brown, crystalline mass, which rapidly deliquesces in the air It dissolves readily in alcohol and ether.

Gold chloride forms beautifully crystallized double salts with many metallic chlorides, *e.g.*, $AuCl_3.KCl + 2\frac{1}{2}H_2O$ and $AuCl_3.NH_4Cl + H_2O$. When auric chloride is heated with magnesium oxide a brown precipitate is obtained, from which all the magnesia is removed by concentrated nitric acid, leaving **Auric Oxide** (Au_2O_3). This is a brown powder which decomposes, near 250°, into gold and oxygen. If the precipitate containing the magnesia be treated, not with concentrated, but with dilute nitric acid, **Auric Hydroxide**—$Au(OH)_3$—remains as a yellowish-red powder. Both the oxide and hydroxide are insoluble in water and acids; they possess, however, acid properties, and dissolve in alkalies. Therefore the hydroxide is also called *auric acid.* Its salts, the aurates, are constituted according to the formula $\overset{I}{Me}AuO_2$, and are derived from the meta-acid, $HAuO_2 = HO.AuO$.

Potassium Aurate—$KAuO_2 + 3H_2O$—crystallizes in bright yellow needles, from a potassium hydroxide solution of auric oxide. These are readily soluble in water; the solution reacts alkaline. The corresponding aurates are precipitated from this solution by many metallic salts, *e.g.* :—

$$KAuO_2 + AgNO_3 = AgAuO_2 + KNO_3.$$

The precipitate produced by magnesia in a solution of auric chloride (see above) consists of magnesium aurate $(AuO_2)_2Mg$. Oxygen salts of auric oxide are not known.

Auric Sulphide—Au_2S_3—is precipitated as a blackish-brown compound, from gold solutions, by hydrogen sulphide. It dissolves in alkaline sulphides with formation of sulpho-salts.

Stannous chloride ($SnCl_2$) added to an auric chloride solution produces, under certain conditions, a purple-brown precipitate, purple of Cassius, which is employed in glass and porcelain painting. Alumina and magnesia yield similar purples, and it appears that their red coloration is due to finely divided metallic gold.

On pouring ammonium hydroxide over auric oxide a brown compound is produced—*fulminating gold.* When this is dried and heated or struck a blow, it explodes very violently.

METALS OF GROUP III.

The triatomic elements, affording derivatives mainly of the form MeX_3, belong to group III of the periodic system (p. 248) :—

		Sc = 44.1	Y = 88.7	La = 138.5	Yb = 173.2
B = 10.9	Al = 27.0				
		Ga = 69.9	In = 113.7	——	Tl = 204.1

These bear the same relations to each other as do the elements of group II (p. 303). Boron has the lowest atomic weight, and the basic, metallic character in it is reduced very much or does not appear at all. In its exclusively acidic hydroxide, $B(OH)_3$, it approaches the metalloids, and is therefore treated with them (p. 243).

Aluminium is a perfect metal; its hydroxide, $Al(OH)_3$, exhibits a predominating basic character, and yields salts with acids. Its relations to boron are like those of silicon to carbon, or of magnesium to beryllium. The connection of aluminium and boron with the same group plainly shows itself in the entire character of the free elements, and in their compounds. Thus aluminium and boron are not dissolved by nitric acid, but by boiling alkalies:—

$$Al + 3KOH = Al(OK)_3 + 3H.$$

There is only a gradual difference between their hydrates. Boron hydroxide, $B(OH)_3$, not only acts as a feeble acid, but we also find that aluminium hydroxide manifests an acidic character, inasmuch as it is capable (p. 333) of forming metallic salts with strong bases (chiefly the alkalies); but owing to the higher atomic weight of aluminium the basic character exceeds the acidic. The similarity is also shown by the existence of perfectly analogous compounds; thus, *e. g.*, the chlorides BCl_3 and $AlCl_3$ can unite with PCl_5 and $POCl_3$.

Scandium, yttrium, lanthanum and ytterbium attach themselves to aluminium as the *first sub-group*. These constitute the third members of the great periods, and hence exhibit a pronounced basic character. As light metals, they are very similar to aluminium in their compounds, so that they all are embraced in one group, which (corresponding to the earthy nature of their oxides) is designated the *Group of Earth Metals*. Cerium and didymium bear a peculiar relation to lanthanum; their atomic weights are nearly alike and their properties very similar. Their apparently abnormal existence is explained by the fact that the 5th period (series 7 and 8), which is very incomplete, shows a somewhat varying function in its intermediate members (p. 250). The metals, erbium, terbium, thulium, and samarium, of recent discovery and but little characterized, may probably also be included in the same period.

The *second sub-group* is more distinctly characterized and accurately investigated; it consists of the heavy metals, gallium, indium and thallium. These belong to the right side of the great periods, possess, therefore, a less basic character, and bear the same relation to each other as Zn, Cd and Hg.*

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* Consult p. 255 upon the behavior of the oxides of this group when heated with metallic magnesium.

Aluminium was formerly classed together with chromium, iron, manganese, cobalt and nickel, in one group, because they all afford sesquioxides, Me_2O_3, whose salts are very much alike. Another fact which was thought to give weight to this classification was the existence of the similarly constituted alums:—

$$(SO_4)_3Al_2SO_4K_2 + 24H_2O \qquad (SO_4)_3Fe_2SO_4K_2 + 24H_2O.$$

Potassium aluminium sulphate. Potassium iron alum.

In its entire behavior, aluminium is, however, very essentially distinguished from the other metals here mentioned—by the acid nature of its hydrate, $Al(OH)_3$—and by its inability to form higher or lower combination forms, while the others yield basic monoxides, MeO, and acid-forming trioxides (CrO_3, FeO_3, MnO_3). Here, again, the similarity of the sesquioxide compounds, Me_2O_3, like those of the monoxide derivatives, is to be regarded as mainly influenced by the similarity of the combination forms (p. 333).

At present aluminium is assumed to be trivalent and this fact apparently contradicts the circumstance that not the simple formulas, $AlCl_3$, $AlBr_3$, but the double ones, Al_2Cl_6, Al_2Br_6, fall to its halogen derivatives (the result of vapor density determinations). On the other hand, however, the so-called metallo-organic compounds of aluminium exist, whose molecules are constituted according to the formulas, $Al(CH_3)_3$, $Al(C_2H_5)_3$; these undoubtedly prove the trivalence of aluminium, because the compounds with hydrocarbon groups (like those with hydrogen) afford the surest guide for the deduction of the valence (p. 251). The existence of the molecules, Al_2Cl_6, Al_2Br_6, etc., does not prove anything against its being a triad, but must be explained by a polymerization of the simple chemical molecules, $AlCl_3$, $AlBr_3$. At higher temperatures the vapor density of aluminium chloride corresponds to the formula $AlCl_3$. We find the same to be the case with arsenious oxide, As_2O_3, and antimony trioxide, Sb_2O_3, whose molecules in vapor form correspond to the doubled formulas, As_4O_6 ($= As_2O_3, As_2O_3$) and Sb_4O_6; and with stannous chloride, whose molecule in vapor form at low temperature is Sn_2Cl_4, but higher it becomes $SnCl_2$, or with gallium chloride that possesses the formulas, $GaCl_3$ and Ga_2Cl_6 (p. 343).

GROUP OF THE EARTH METALS.

ALUMINIUM.

$Al = 27.08$.

This is one of the most widely distributed elements. As oxide, it crystallizes as ruby, sapphire and corundum; less pure as emery. It is commonly found as aluminium silicate (clay, kaolin), and in combination with other silicates, as feldspar, mica, and also in most crystalline rocks. It occurs, too, united with fluorine and sodium, as cryolite, in large deposits, in Iceland.

Metallic aluminium is obtained by igniting the chloride, or, better, the double chloride of sodium and aluminium with metallic sodium:—

$$AlCl_3.NaCl + 3Na = Al + 4NaCl.$$

The metal may also be prepared by electrical processes. In the Hall method cryolite, or an electrolyte of analogous composition, is electrolyzed, the bath being constantly kept saturated with alumina. The aluminium in the end separates at the negative pole. In the Cowles process the underlying principle is the interruption of a powerful electric current, the formation of an immense arc, and the reduction in the arc of the aluminium oxide, by carbon, in the presence of the metal.

It is a silver-white metal of strong lustre, is very ductile, and may be drawn out into fine wire and beaten into thin leaflets. Its specific gravity is 2.583; it belongs, consequently, to the light metals and possesses, therefore, all the properties opposed to those of the heavy metals (see p. 314). It fuses at a red heat but will not vaporize. It changes very little in the air at ordinary temperatures, and even when heated. If, however, thin leaves be heated in a stream of oxygen, they will burn with a bright light. Nitric acid does not affect aluminium; sulphuric acid only dissolves it on boiling, while it is readily soluble, even in the cold, in hydrochloric acid. It dissolves in potassium and sodium hydroxide, with evolution of H, and forms aluminates:—

$$Al + 3KOH = K_3AlO_3 + 3H.$$

Owing to its stability in air and beautiful lustre, aluminium is sometimes employed for vessels and ornaments. The alloy of copper with 10–12 per cent. aluminium is distinguished by its great hardness and durability. It may be poured into moulds, and possesses a gold-like color and lustre. Under the name of aluminium bronze, it is used for the composition of various articles, as watches, spoons, etc.

Its firmness and elasticity render it suitable for physical instruments (arms of balances) and watch springs.

Aluminium affords compounds of the form AlX_3, or Al_2X_6 (p. 350) exclusively. Its salts, soluble in water, have an acid reaction, and a sweet, astringent taste.

The heat of formation of some of the aluminium compounds equals:—

$(Al_2,Cl_6) = 321.8.$ $(Al_2,Br_6) = 239.3.$ $(Al_2,I_6) = 140.6.$
$(Al_2,Cl_6,Aq.) = 475.5.$ $(Al_2,Br_6,Aq.) = 409.9.$ $(Al_2,I_6,Aq.) = 318.6.$
$(Al_2,O_3,3H_2O) = 388.8.$

The heat evolved in the formation of a quantity of aluminium hydroxide, corresponding to one atom of oxygen, is 129.6; since that of water is far less ($H_2,O = 69.0$), it must be decomposed by aluminium, with liberation of hydrogen (p. 279). If this does not transpire under ordinary conditions, the reason must be sought for in the insolubility of aluminium hydroxide. Indeed, the reaction occurs if aluminium chloride, or another salt, in which the aluminium oxide is soluble, be added to the water. Conversely, the high heat of formation of aluminium oxide explains why it is not reduced by carbon.

Aluminium Chloride, $AlCl_3$, or Al_2Cl_6, is produced by the action of chlorine upon heated aluminium: also by heating a mixture of aluminium oxide and carbon in a current of chlorine:—

$$Al_2O_3 + 3C + 6Cl = Al_2Cl_6 + 3CO.$$

Chlorine and carbon do not act separately upon the oxide; by their mutual action, however, the reaction occurs in consequence of the affinity of carbon for oxygen, and of chlorine for aluminium. The oxides of boron and silicon show a similar deportment.

Aluminium chloride may be obtained in white, hexagonal leaflets by sublimation. It sublimes readily, but will only fuse when subjected to high pressure. Deville and Troost (1857) first determined the vapor density of aluminium chloride, bromide, and iodide at 440°, and found it to correspond to the formulas Al_2Cl_6, Al_2Br_6, and Al_2I_6. This led to the supposition that aluminium was quadrivalent in all its compounds. The most recent investigations of Nilson and Petterson have shown that at higher temperatures (above 700°) the vapor density of the chloride corresponds to the formula $AlCl_3$.

Aluminium chloride absorbs moisture from the air, and deliquesces. It crystallizes from a concentrated hydrochloric acid solution, with 6 molecules of water. On evaporating the aqueous solution, the chloride decomposes into aluminium oxide and hydrogen chloride :—

$$Al_2Cl_6 + 3H_2O = Al_2O_3 + 6HCl.$$

It forms double chlorides with many metallic chlorides, viz.: $AlCl_3.NaCl$, $AlCl_3.KCl$. The solutions of these may be evaporated to dryness without decomposition. It also unites with many halogen derivatives of the metalloids :—

$$AlCl_3.PCl_5,\ AlCl_3.POCl_3,\ AlCl_3.SCl_4.$$

Aluminium Bromide—Al_2Br_6—is obtained like the chloride, and consists of shining leaflets which fuse at 90° and boil at 265-270°. Its vapor density is 267.4 ($H = 1$), corresponding to the formula Al_2Br_6. It behaves like the chloride.

Aluminium Iodide—Al_2I_6—is formed on heating aluminium filings with iodine. It is a white, crystalline mass, fusing at 185°, and boiling about 400°. It is best prepared by covering sheet aluminium with carbon disulphide, and then adding the calculated amount of iodine gradually, letting the whole stand for some time, and then distilling off the CS_2. The reaction occurring between aluminium iodide and oxygen is interesting. If the vapor of the former be mixed with the latter, and then brought in contact with a flame, or if acted upon by an electric spark, a violent detonation will ensue; aluminium oxide and iodine result:—

$$Al_2I_6 + 3O = Al_2O_3 + 6I.$$

This deportment is due to the great difference in the heats of formation of the aluminium oxide (about 380 C.), and the iodide (140.6 C.). The chloride and bromide are similarly decomposed, but with less violence.

Aluminium Fluoride—$AlFl_3$ or Al_2Fl_6—obtained by conducting hydrogen fluoride over heated aluminium oxide or hydroxide, sublimes at a red heat in colorless rhombohedra. It is insoluble in water, unaltered by acids, and is very stable. It yields insoluble double fluorides with alkaline fluorides. The compound—$AlFl_3.3NaFl$—occurs in Greenland, in large deposits, as cryolite, and is employed in the soda manufacture (p. 295).

Aluminium Oxide—Al_2O_3—is found crystallized in hexagonal prisms in nature, as ruby, sapphire, and corundum, colored by other admixtures. Impure corundum, containing aluminium and iron oxides, is called emery, and serves for polishing glass. The specific gravity of these minerals is 3.9; their hardness is only a little below that of the diamond. Artificial aluminium oxide may be obtained by igniting the hydroxide, and is a white amorphous powder, which fuses to a transparent glass in the oxy-hydrogen flame. A mixture of aluminium fluoride, and boron trioxide, heated to a white heat has the boron fluoride volatilized, and crystallized aluminium oxide remains :—

$$Al_2Fl_6 + B_2O_3 = Al_2O_3 + 2BFl_3.$$

The crystallized or strongly ignited aluminium oxide is almost insoluble in acids; to decompose it, it is fused with caustic alkalies or with primary potassium sulphate—$HKSO_4$.

Aluminium Hydroxides.—The *normal hydroxide*, $Al(OH)_3$ or $Al_2(OH)_6$, occurs in nature as hydrargillite. The hydroxide, $Al_2O_2(OH)_2$, is diaspore. Bauxite is a mixture of the hydroxide, $Al_2O(OH)_4$, with ferric oxide. The normal hydroxide is artificially obtained as a white voluminous precipitate, by adding ammonium hydroxide or an alkaline carbonate (in latter case carbon dioxide escapes, p. 355) to a soluble aluminium salt. Freshly precipitated, it dissolves in acids and in potassium and sodium hydroxides. By long standing under water, or after drying, it is, without any alteration in composition, difficultly soluble in acids. When carefully heated, the normal hydroxide first passes into AlO.OH.

The freshly precipitated hydroxide dissolves readily in a solution of aluminium chloride or acetate. On dialyzing (p. 240) this solution the aluminium salt or crystalloid diffuses, and in the dialyzer remains the pure aqueous solution of the hydroxide. This has a faint alkaline reaction and is coagulated by slight quantities of acid, alkalies and many salts; the soluble hydrate passes into the insoluble gelatinous modification.

Gelatinous aluminium hydroxide possesses the property of precipitating many dyestuffs from their solutions, forming colored insoluble compounds (lakes) with them. On this is based the application of aluminium hydroxide as a mordant in dyeing. The acetate is generally used for this purpose. Goods saturated with this salt are heated with steam, which causes the decomposition of the weak acetate; acetic acid escapes, while the separated aluminium hydroxide sets itself upon the fibre of the material. If the latter now be introduced into the solution of coloring matter the latter is fixed by the aluminium hydroxide upon the fibre. At present, sodium aluminate is employed instead of the acetate.

Aluminium hydroxide has a feeble acid character, and can form salt-like compounds with strong bases. On carefully evaporating its solution in sodium or potassium hydroxide, or upon addition of alcohol, white amorphous compounds of $KAlO_2$, $NaAlO_2$ and $(NaO)_3Al$ are obtained. The potassium compound can be obtained in crystalline form. These derivatives, known as *aluminates*, are not very stable, and are even decomposed by carbon dioxide, with elimination of aluminium hydroxide :—

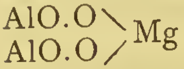
$$2AlO_2Na + CO_2 + 3H_2O = Al_2(OH)_6 + CO_3Na_2.$$

The aluminium hydroxide obtained in this manner, in distinction from that precipitated from acid aluminium solutions by the alkalies, is not gelatinous, and is more difficultly soluble in acids, especially acetic. It comprises the ordinary alumina of commerce.

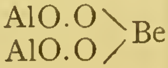
On adding calcium chloride, strontium chloride, or barium chloride to the solution of potassium or sodium aluminate, white insoluble aluminates are precipitated :—

$$2AlO_2Na + CaCl_2 = (AlO_2)_2Ca + 2NaCl.$$

Similar aluminates frequently occur as crystallized minerals, in nature. Thus the spinels consist chiefly of magnesium aluminate,

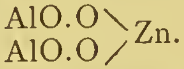


$\left.\begin{matrix}AlO.O\diagdown\\ AlO.O\diagup\end{matrix}Mg\right.$; chrysoberyl is beryllium aluminate,



$\left.\begin{matrix}AlO.O\diagdown\\ AlO.O\diagup\end{matrix}Be\right.$;

gahnite is zinc aluminate,



$\left.\begin{matrix}AlO.O\diagdown\\ AlO.O\diagup\end{matrix}Zn\right.$.

Nearly all these minerals, commonly called spinels, crystallize in regular octahedrons, like the corresponding chromium compounds (see these); the exceptions are chrysoberyl, crystallizing in the rhombic system, and hausmannite, Mn_3O_4, in the quadratic system.

Technically, alumina is obtained from cryolite, bauxite and other minerals containing aluminium. The pulverized bauxite is heated with dry sodium carbonate in furnaces, and the resulting sodium aluminate extracted with water. From the clear solution carbon dioxide precipitates the hydroxide, while sodium carbonate remains dissolved, and is afterward recovered. The dried aluminium hydroxide occurs as a white powder in trade.

The gelatinous, readily soluble (colloidal) aluminium hydroxide (see above) precipitated from acid solutions by alkalies, has lately been prepared upon a large scale, according to the method of Löwig, by treating the sodium aluminate solution with milk of lime; calcium aluminate precipitates, while sodium hydroxide remains in solution :—

$$2AlO_2Na + Ca(OH)_2 = (AlO_2)_2Ca + 2NaOH.$$

The calcium aluminate is dissolved in hydrochloric acid :—

$$(AlO_2)_2Ca + 8HCl = 2AlCl_3 + CaCl_2 + 4H_2O,$$

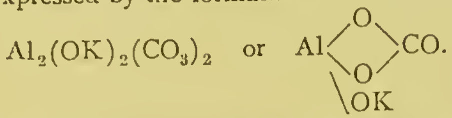
and to the solution now containing the alumina as chloride the corresponding amount of calcium aluminate added, and aluminium hydroxide is precipitated :—

$$2AlCl_3 + 3(AlO_2)_2Ca = 4Al_2O_3 + 3CaCl_2.$$

According to this procedure, the sodium hydroxide formed in the first reaction is obtained together with the alumina. On conducting carbon dioxide into a solution of alkaline carbonates, and adding a solution of an alkaline aluminate at the same time, white *aluminium-alkali carbonates* are precipitated :—

$$Al_2O_3.K_2O + 2CO_3NaH = Al_2O_3.K_2O.2CO_2 + 2NaOH.$$

The caustic alkali that is formed in this way is converted again into bicarbonate by carbon dioxide. In a dry state the precipitates are white, chalk-like masses which at 90° contain 5 molecules of water: $Al_2O_3.K_2O.2CO_2 + 5H_2O$. Their constitution may be expressed by the formula:—



$$Al_2(OK)_2(CO_3)_2 \quad \text{or} \quad Al\begin{matrix}\diagup O \diagdown \\ \diagdown O \diagup \\ \diagdown OK\end{matrix}CO.$$

They dissolve readily in dilute acids, even acetic, with evolution of carbon dioxide, and are suitable for the preparation of pure alumina mordants and antiseptic solutions (Lõwig).

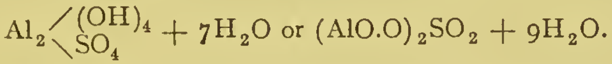
The basic character of aluminium hydroxide exceeds the acid; but it is so feeble that it is not capable of forming salts with weak acids, as carbon dioxide, sulphurous acid, and hydrogen sulphide. When sodium carbonate is added to solutions of aluminium salts, aluminium hydroxide is precipitated, while carbon dioxide is set free:—

$$Al_2Cl_6 + 3Na_2CO_3 + 3H_2O = Al_2(OH)_6 + 6NaCl + 3CO_2.$$

The alkaline sulphides behave similarly:—

$$Al_2Cl_6 + 3(NH_4)_2S + 6H_2O = Al_2(OH)_6 + 6NH_4Cl + 3H_2S.$$

Aluminium Sulphate—$Al_2(SO_4)_3$—crystallizes from aqueous solution with 18 molecules of H_2O in thin leaflets with pearly lustre. These dissolve readily in water; when heated, they melt and lose all their water of crystallization. The sulphate is obtained by dissolving the hydroxide in sulphuric acid, or by the decomposition of pure clay with the same acid; the residual silicic acid is removed by filtration, and the solution of the sulphate evaporated. When a quantity of ammonium hydroxide, insufficient for complete precipitation, is added to the sulphate, *basic* sulphates separate out. Salts similar to the latter are also found in nature; thus, aluminite, used to prepare alum, has the composition:—

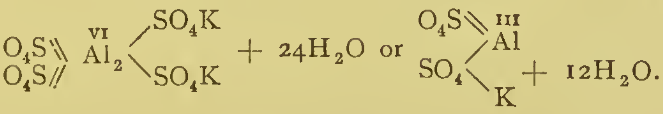


$$Al_2\begin{matrix}\diagup (OH)_4\\ \diagdown SO_4\end{matrix} + 7H_2O \text{ or } (AlO.O)_2SO_2 + 9H_2O.$$

Aluminium sulphate can combine with the alkaline sulphates and affords double salts, termed *alums*, *e. g.*, potassium alum:—

$$(SO_4)_3Al_2.SO_4K_2 + 24H_2O \text{ or } (SO_4)_2AlK + 12H_2O.$$

Their constitution is expressed by the following formula:



$$\begin{matrix}O_4S\diagdown\!\diagdown\\ O_4S/\!/\end{matrix}\overset{VI}{Al_2}\begin{matrix}\diagup SO_4K\\ \diagdown SO_4K\end{matrix} + 24H_2O \text{ or } \begin{matrix}O_4S\diagdown\!\diagdown \overset{III}{Al}\\ SO_4\diagup\\ \diagdown K\end{matrix} + 12H_2O.$$

In this compound the potassium may be replaced by sodium, ammonium, rubidium, cæsium, and also by thallium. Iron, chromium and manganese afford like derivatives:—

$Fe_2(SO_4)_3.K_2SO_4 + 24H_2O$ Potassium iron alum.

$Mn_2(SO_4)_3. Na_2(SO)_4 + 24H_2O$. Sodium manganese alum.

All these alums crystallize in regular octahedra or cubes, and can form isomorphous mixtures.

The most important of them is *Potassium Aluminium Sulphate* or *ordinary alum*, $AlK(SO_4)_2 + 12H_2O$. It crystallizes from water in large, transparent octahedra, soluble in 8 parts water of ordinary temperature, or in ⅓ part boiling water. The solution has an acid reaction and a sweetish, astringent taste. When placed over sulphuric acid, alum loses 9 (or 18) molecules of H_2O. When heated it melts in its water of crystallization, loses all the latter and becomes a white, voluminous mass—*burnt alum*. Upon adding a little sodium or potassium carbonate to a hot alum solution the hydroxide first produced dissolves, and when the liquid cools, the alum crystallizes out in cubes, as *cubical alum*. The addition of more sodium carbonate causes the precipitation of the basic salt—$AlK(SO_4)_2.Al(OH)_3$. Alunite, found in large quantities near Rome and Hungary, has a similar composition $(SO_4)_2(AlO)_3K + 3H_2O$.

Commercial alum is obtained according to various methods: 1. From alunite, by heating and extracting with hot water. In this way alum dissolves while the hydroxide remains; from such solutions the former crystallizes in combinations of the octahedron with cube faces—Roman alum. 2. The most common source of alum was formerly *alum shale*, a clay containing pyrite and peat. This is roasted and after moistening with water is exposed for a long time to the action of the air. By this means FeS_2 is converted into $FeSO_4$ and free sulphuric acid, which, acting upon the clay, forms aluminium sulphate. The mass is extracted with water, potassium sulphate added, and the whole permitted to crystallize. 3. At present clay is treated directly with sulphuric acid, and to the solution of aluminium sulphate potassium or ammonium sulphate is added. 4. Bauxite and cryolite are admirable material for the preparation of alum. The working of cryolite for alumina and soda is described on p. 295, and that of bauxite, p. 354.

Ammonium Alum—$(SO_4)_2AlNH_4 + 12H_2O$—crystallizes, like potassium alum, in large crystals, and at present, owing to its cheapness, is applied almost exclusively for technical purposes. Sodium alum is much more soluble, and crystallizes with difficulty. As the alum employed in dyeing must contain no iron, we understand why this salt is not applicable. At present the alum is being more and more supplanted by aluminium sulphate and sodium aluminate in all practical operations, because these chemicals can be procured perfectly free from iron.

Aluminium Phosphate—$AlPO_4 + 4H_2O$—is thrown out of aluminium salt solutions by sodium phosphate, as a white gelatinous precipitate; this is readily soluble in acids, acetic excepted.

Aluminium Silicates.—The most important of the aluminium double silicates, so widely distributed in nature, are: *leucite*, $(SiO_3)_2AlK$, *albite* or soda feldspar, Si_3O_8AlNa, ordinary feldspar—orthoclase—$AlKSi_3O_8$—and the various micas, which, with quartz, compose granite. When these disintegrate under the influence of water and the carbon dioxide of the air, alkaline silicates are dissolved and carried away by water, while the insoluble aluminium silicate, *clay*, remains. Perfectly pure clay is white, and is called *kaolin*, or porcelain clay; its composition mostly corresponds to the formula, $Al_2(SiO_3)_3Al_2O_5H_4$, or $Si_2O_9Al_2H_4$. When clay is mixed with water a tough kneadable mass is obtained. By drying and burning, it becomes compact and hard, and is the more fire-proof, the purer the clay. On this depends the use of clay for the manufacture of earthenware, from the red brick to porcelain.

To produce porcelain a very fine mixture of kaolin, feldspar and quartz is employed. On strong ignition, the feldspar fuses, fills the pores of the clay and thus furnishes a fused transparent mass—porcelain. When it is not so strongly ignited, it remains porous—faience—serving for finer clay vessels. To render these impervious to water, they are covered with glazing. This consists of various readily fusible silicates. Rough earthenware vessels are constructed from impure clay, and they are usually glazed by throwing salt into the ovens at the time of burning. The hot steam decomposes the salt into hydrochloric acid and sodium hydroxide, which forms an easily fusible silicate on the surface of the clay.

Ultramarine.—The rare mineral *Lapis lazuli*, which was formerly employed as a very valuable blue color under the name of *Ultramarine*, is a compound of aluminium sodium silicate with sodium polysulphides. At present ultramarine is prepared artificially, in large quantities, by heating a mixture of clay, dry soda (or sodium sulphate), sulphur and wood ashes, away from air. *Green* ultramarine is the product. This is then washed with water, dried, mixed with powdered sulphur and gently heated with air contact until the desired blue color has appeared—*blue* ultramarine. The cause of the blue coloration is generally assumed to be due to the existence of a complicated sulphur compound, whose nature is not yet explained. On pouring hydrochloric acid over the blue product, the color disappears with liberation of sulphur and hydrogen sulphide—this would point to the existence of a polysulphide. Violet and red ultramarines are prepared at present by conducting dry hydrogen chloride gas and air over common ultramarine at 100–150°.

RARE METALS.

In some very rare minerals, like cerite, gadolinite, euxenite, and orthite, occurring principally in Sweden and Greenland, is found a series of metals which, in their entire deportment, closely resemble aluminium (p. 349). These are scandium, yttrium, cerium, lanthanum, didymium, ytterbium, and the more recent erbium, terbium, thulium, samarium, and holmium (Soret's X element). These generally form difficultly soluble oxalates, and are, therefore, precipitated from solution by oxalic acid. They also afford difficultly soluble sulphates and double sulphates, of which the potassium double salts are constituted, according to the formula, $Me_2(SO_4)_3.3K_2SO_4$. The different decomposability of their nitrates upon application of heat affords an excellent means for their isolation and separation.

Scandium, yttrium, lanthanum, cerium, and ytterbium have been most accurately investigated. Their atomic weights are very approximately correct. The most interesting of the group is scandium, atomic weight 44. It fills out the gap between calcium and titanium. It coincides in all its properties with those deduced theoretically from the periodic system by Mendelejeff for the element *ekaboron* (compare Gallium).

Other elements have been observed whose salt solutions possess the remarkable property of yielding absorption spectra. They are didymium, erbium, samarium (decipium), holmium, and thulium. Nilson, Krüss, and other investigators regard them as complex mixtures, consisting of several elements that have not yet been isolated.

Scandium—$Sc = 44$—contained in euxenite and gadolinite, has not yet been obtained in a free condition. Its *oxide*, Sc_2O_3, is obtained by igniting the hydroxide or nitrate, and is a white, infusible powder (like magnesia and oxide of beryllium). Its specific gravity equals 3.86; the specific heat 0.1530. The *hydroxide*, $Sc(OH)_3$, is precipitated as a gelatinous mass from its salts by the alkalies, and is insoluble in an excess of the latter. The *nitrate* crystallizes in little prisms, and is decomposed with difficulty by heat. The *potassium double sulphate*, $Sc_2(SO_4)_3.3K_2SO_4$, is soluble in warm water, but not in a solution of potassium sulphate. The chloride affords a characteristic spark spectrum.

Yttrium—$Y = 89$—has long been known in its compounds, but has never been investigated in a pure condition. Its chief source is gadolinite (upward of 35 per cent.). Its *potassium double sulphate* is soluble in a potassium sulphate solution, and in this manner it can be readily separated from cerium, lanthanum, and didymium. Its *nitrate* is much more difficult to decompose than those of scandium and ytterbium. The *chloride*, $YCl_3 + 7H_2O$, forms large prisms, and gives a spark spectrum.

Lanthanum—$La = 138.2$—separated from its chloride by electrolysis, resembles iron as regards color and lustre, oxidizes in the air, and burns in a flame with a bright light. Its specific gravity equals 6.16, the specific heat 0.0448. The *hydroxide*, $La(OH)_3$, is precipitated as a gelatinous mass, and reacts alkaline. Its chloride shows a distinct spark spectrum. The metal forms a *hydride* (p. 255).

Cerium—$Ce = 140$—occurs in cerite (60 per cent.), and is also obtained by the electrolysis of the chloride. It is very similar to lanthanum, but at ordinary temperatures is more stable than the latter; burns much more readily, so that broken-off particles of it inflame of their own accord. The specific gravity of the fused metal is 6.72, the specific heat 0.0448. Besides the salts of the *sesquioxide*, Ce_2O_3, it forms some from the *dioxide*, CeO_2. The first are colorless, while the latter are colored yellow or brown; red ceric hydroxide, $Ce(OH)_4$, is precipitated from the first, on the addition of hypochlorites. A little aqueous hydrofluoric acid will convert the ceric hydroxide into *cerium tetrafluoride*. These compounds indicate that cerium is tetravalent and that it probably belongs to the fourth group of the periodic system (p. 249). Compare also p. 255.

Ytterbium—Yb=173.—Its *oxide*, Yb_2O_3, is obtained from the so-called erbium earth (from euxenite and gadolinite) by repeated partial heating of the mixed nitrates, whereby the scandium nitrate is the first to decompose. It is a white infusible powder, of specific gravity 9.17; its specific heat is 0.0646. The salts of ytterbium are colorless, and show no absorption spectrum.

Terbium—Tr = 150.—*Terbium oxide*, Tr_2O_3, occurs in large amount in samarskite. It has an orange-yellow color, resembles the oxide of erbium, but does not show an absorption spectrum.

THE GALLIUM GROUP.

The three heavy metals, gallium, indium, and thallium, bear the same relations to aluminium that we see exhibited by Cu, Ag, and Au to sodium, Na, and Zn, Cd, and Hg to magnesium.

Cu	63.3	Zn	65.5	Ga	69.9	Ge	72.3	As	75.0
Ag	107.938	Cd	112.1	In	113.7	Sn	118.1	Sb	120.3
Au	197.2	Hg	200.4	Tl	204.1	Pb	206.91	Bi	208.

They constitute the corresponding members of the three great periods; and as second sub-group attach themselves to aluminium, while cerite metals form the first, more basic group (p. 349). The entire character of the three elements under consideration is influenced by this position in the periodic system, because regular relations appear in all directions, as may be observed, for example, in the specific gravities, fusing points, and other physical properties in the free metals:—

	Ga	In	Tl
Atomic weight	69.9	113.7	204.1
Specific gravity	5.9	7.4	11.8
Fusing point	30°	176°	290°

Being members of group III of the periodic system, Ga, In, and Tl yield compounds of the trivalent form, and these are analogous to those of aluminium in many respects. Consult p. 255.

Thallium, like other elements with high atomic weight (Au, Hg, Pb), exhibits great variations from the group properties (p. 325). It yields, for example, not only derivatives of the form TlX_3, but also those of TlX. If we include thallium as a member of the last great period (Pt, Au, Hg, Tl, Pb, Bi), we will discover that, as in case of the other metals of this series, a remarkable regularity underlies all its forms of combinations—the highest as well as the lowest:—

$PtCl_2$	$AuCl$	$HgCl$	$TlCl$	$PbCl_2$	$BiCl_3$
$PtCl_4$	$AuCl_3$	$HgCl_2$	$TlCl_3$	$PbCl_4$	BiX_5.

1. GALLIUM.

$Ga = 69.9$.

Gallium was discovered in zinc blende from Pierrefitte, in 1875, by Lecoq de Boisbaudran, by means of the spectroscope. As early as the year 1870, Mendelejeff, taking the table of the periodic system devised by him as basis, predicted the existence of a metal (standing between aluminium and indium, with an atomic weight of nearly 69), which he named *Eka-aluminium.* Its properties were necessarily deduced from its position in the periodic system. All the properties of gallium known at that time agreed with those of eka-aluminium, and it seemed very probable that this element, which had been theoretically established, was in reality gallium. This is now confirmed by the fact that the atomic weight, determined by experiment, agrees with that deduced theoretically.

As yet gallium has only been found in very small quantity, and is but imperfectly investigated. It is characterized by a spectrum consisting of two violet lines. Separated by electrolysis from an ammoniacal solution of its sulphate, it is a white, hard metal, of specific gravity 5.9, with a fusing point 30°. It is only superficially oxidized in the air, not altered by water, and is not volatile up to a red heat. Like aluminium, it is scarcely attacked by nitric acid, but dissolves readily in hydrochloric acid.

Gallium Oxide—Ga_2O_3—is obtained by igniting the nitrate. It is a white mass which sublimes when heated in a current of hydrogen. The **hydroxide**—$Ga(OH)_3$—is thrown out of solutions of its salts by the alkalies as a white flocculent precipitate, readily soluble in an excess of the precipitant, but rather difficultly soluble in ammonium hydroxide.

Gallium Chloride—$GaCl_3$—is produced on heating gallium in a current of chlorine gas; it forms colorless crystals that fuse at 75°, sublime about 60° and boil at 215–220°. Its vapor density at 440° corresponds to the formula $GaCl_3$, at 270° very closely to Ga_2Cl_6. The chloride *fumes in the air*, like aluminium chloride, deliquesces and decomposes in the evaporation of its aqueous solution.

Gallium Nitrate—$Ga(NO_3)_3$, and **Gallium Sulphate**, $Ga_2(SO_4)_3$—are crystalline and very deliquescent. The latter forms a double salt with ammonium sulphate—similar to the alums:—

$$(SO_4)_3\,Ga_2.SO_4(NH_4)_2 + 24H_2O.$$

Hydrogen sulphide only precipitates gallium from acetate solutions.

2. INDIUM.

$In = 113.7$.

Owing to its resemblance to zinc, indium was regarded as a divalent metal, and its compounds composed according to the formula, InX_2; this fixed its atomic weight at 75.6. The specific heat, however, made the atomic weight one and a half times as large (p. 262). Hence it is trivalent and its derivatives are constituted according to the form, InX_3. It belongs to the group of aluminium, and, in its derivatives, manifests some similarity to this metal.

It was discovered, in 1863, by Reich and Richter, by the aid of spectrum analysis. Its spectrum is characterized by a very bright indigo-blue line, hence its name. It only occurs in very minute quantities in some zinc blendes from Freiberg and the Hartz.

It is a silver-white, soft and tenacious metal, of specific gravity, 7.42. It fuses at 176° and distils at a white heat. At ordinary temperatures it is not altered in the air; heated, it burns with a blue flame to indium oxide. It is difficultly soluble in hydrochloric and sulphuric acids, but dissolves readily in nitric acid.

Indium Chloride—$InCl_3$—results from the action of chlorine on metallic indium, or upon an ignited mixture of indium oxide, and carbon. It sublimes in white, shining leaflets, which deliquesce in the air. Its vapor density corresponds to the formula $InCl_3$. It does not decompose when its aqueous solution is evaporated.

Indium Oxide—In_2O_3—is a yellow powder resulting from the ignition of the hydroxide.

Indium Hydroxide—$In(OH)_3$—is precipitated as a gelatinous mass, by alkalies, from indium solutions. It is soluble in sodium and potassium hydroxides.

Indium Nitrate—$In(NO_3)_3$—crystallizes with three molecules of water, in white deliquescent needles.

Indium Sulphate—$In_2(SO_4)_3$—remains on evaporating a solution of indium in sulphuric acid as a gelatinous mass, with three molecules of water. It forms an alum with ammonium sulphate.

Indium Sulphide—In_2S_3—is precipitated by hydrogen sulphide as a yellow-colored compound from indium solutions.

Indium also forms a dichloride and monochloride.

Indium Dichloride—$InCl_2$—is produced when metallic indium is heated in a current of hydrogen chloride. It is a white crystalline mass, which on exposure to a more intense heat becomes a yellow liquid and sublimes. Its vapor density at 1000°–1040° corresponds to the formula $InCl_2$. Water decomposes it at once into indium trichloride and metallic indium: $3InCl_2 = 2InCl_3 + In$.

Indium Monochloride—$InCl$—like gallium dichloride (p. 360), results when the dichloride is heated with metallic indium. It is a crystalline, reddish yellow mass, which has a reddish black color when fused. Its vapor density at 1100°–1400° corresponds to the formula InCl. Water decomposes it into the trichloride and metallic indium: $3InCl = InCl_3 + 2In$.

3. THALLIUM.

$Tl = 204.1.$

Thallium is rather widely distributed in nature, but in very small quantity. The very rare mineral *crookesite* contains 17 per cent. of the metal, together with copper, selenium and silver. It is often found with potassium in sylvite and carnallite, in mineral springs, and in some varieties of pyrite and zincblendes. When these pyrites are roasted for the production of sulphuric acid, according to the chamber process, the thallium deposits as soot in the chimney and in the chamber sludge, and was discovered in the latter, in 1863, almost simultaneously, by Crookes and Lamy, by means of the spectroscope.

To get the thallium, the chimney-dust is boiled with water or sulphuric acid, and thallous chloride precipitated from the solution by hydrochloric acid. The chloride is then converted into sulphate, and the metal separated from the latter by means of zinc or the electric current. Thallium is a white metal, as soft as sodium, and has the specific gravity 11.8. It fuses at 290°, and distils at a white heat. It oxidizes very rapidly in moist air. It does not decompose water at ordinary temperatures. It is, therefore, best preserved under water in a closed vessel. By air access it gradually dissolves in the water, forming thallium hydroxide and carbonate. Heated in the air it burns with a beautiful green flame whose spectrum shows a very intense green line, hence the name thallium, from *ϑαλλός*, green. Thallium dissolves readily in sulphuric and nitric acids, but is only slightly attacked by hydrochloric acid, owing to the insolubility of thallous chloride.

Thallium forms two series of compounds: **thallous**—$\overset{I}{Tl}X$ and **thallic**—$\overset{III}{Tl}X_3$. The first are very similar to the compounds of the alkalies (and also to those of silver). The solubility of the hydroxide and carbonate in water shows this; their solutions have an alkaline reaction. Again, many thallous salts are isomorphous with those of potassium, and afford similar double salts. In the insolubility of its sulphur and halogen compounds, monovalent thallium approaches silver and lead.

In its compounds of the form TlX_3 thallium is trivalent, like aluminium, but otherwise shows scarcely any similarity to the latter.

The heat of formation of some of the thallous compounds is:—

$$(Tl_2,O) = 42.2 \qquad (Tl,Cl) = 48.5 \qquad (Tl,Br) = 41.2 \qquad (Tl,I) = 30$$
$$(Tl,O,H) = 56.9 \qquad (Tl_2,S,O_4) = 210.9 \qquad (Tl,N,O_3) = 58.1.$$

The heat of solution of these compounds is negative. From the numbers cited above we can understand the deportment of thallium toward water and the acids. The heat of formation of the *ic* compounds in aqueous solution equals

$$(Tl,Cl_3,Aq.) = 89.0 \qquad (Tl,Br_3,Aq.) = 56.1 \qquad (Tl,I_3,Aq.) = 10.5$$
$$(Tl_2,O_3,3H_2O) = 86.9.$$

THALLOUS COMPOUNDS.

Thallous Oxide—Tl_2O—is formed by the oxidation of thallium in the air, or by heating the hydroxide to 100°. It is a black powder which dissolves in water with formation of the hydroxide.

Thallous Hydroxide—$Tl(OH)$—may be prepared by decomposing thallium sulphate with an equivalent amount of barium hydroxide, and crystallizes with one molecule of water in yellowish prisms. It dissolves readily in water and alcohol, affording strong alkaline solutions.

Thallous Chloride—$TlCl$—is thrown down from solutions of thallous salts by hydrochloric acid as a white, curdy precipitate, which is very difficultly soluble in water. It separates in small crystals from the hot solution. It fuses at 427°, and boils about 715°. Like potassium chloride, it affords an insoluble salt with platinic chloride—$PtCl_4.2TlCl$. *Thallous bromide* forms a white, and *thallous iodide* a yellow precipitate.

Thallous Sulphate—Tl_2SO_4—crystallizes in rhombic prisms, isomorphous with potassium sulphate. It dissolves in 20 parts of water at ordinary temperatures. It affords double salts with the sulphates of the metals of the magnesium group, of ferrous oxide, of cupric oxide, etc. (p. 318), *e. g.*, $MgSO_4.Tl_2SO_4 + 6H_2O$; these are perfectly similar and analogous to the corresponding double salts of potassium and ammonium. It affords thallium alum with the sulphates of the sesquioxides of the iron group, *e. g.*, $AlTl(SO_4)_2 + 12H_2O$; these are similar to potassium alum—$AlK(SO_4)_2 + 12H_2O$.

Thallous Carbonate—Tl_2CO_3— is obtained from the oxide by the absorption of CO_2; it crystallizes in needles, which dissolve at ordinary temperatures in 20 parts of water. The solution has an alkaline reaction.

Thallous Sulphide—Tl_2S—is precipitated from thallous salts by hydrogen sulphide as a black compound, insoluble in water.

THALLIC COMPOUNDS.

Thallic Chloride—$TlCl_3$—is produced by the action of chlorine upon Tl or TlCl in water, and is very soluble in water. It decomposes at 100° into TlCl and Cl_2. The alkalies precipitate from its solutions **thallic hydroxide**, $TlO.OH$, a brown powder, which, at 100°, passes into **thallic oxide**, Tl_2O_3. Further heating decomposes the latter into thallous oxide and oxygen.

The oxide and hydroxide are soluble in hydrochloric, nitric, and sulphuric acids, forming $Tl(NO_3)_3$, $Tl_2(SO_4)_3$, $TlCl_3$.

On conducting chlorine through a solution of thallic hydroxide in potassium hydroxide, it assumes an intense violet color, due probably to the formation of the potassium salt of *thallic acid*, the composition of which is yet unknown.

The thallium compounds are poisonous. They are employed in making thallium glass, which refracts light more strongly than lead glass. The spectrum of the thallium flame shows a very bright green line.

METALS OF THE FOURTH GROUP.

The elements of group IV in the periodic system (p. 249),

Ti = 48.1 Zr = 90.7 (Ce = 140.2) Th = 232.4
C = 12, Si = 28.4 Ge = 72.3 Sn = 118.1 Pb = 206.91,

show the same analogies that were observed with the members of group III (p. 348). Their character is, however, more non-metallic; their derivatives are chiefly of the types MeX_4 and MeO_2, of which the latter are acid (p. 267).

The first two elements, carbon and silicon, with low atomic weights, belong to the two short periods and are true non-metals. Their oxides and hydroxides are acid in nature. The first more basic sub-group comprises titanium, zirconium (cerium), and thorium. They constitute the fourth members of the large periods. Their compounds are almost exclusively of the type MeO_2, are very similar to the silicon derivatives, and are usually discussed with the non-metals after silicon (p. 241). The other sub-group consists of more electro-negative heavy metals: germanium, tin, and lead. These constitute the transition from the elements in group III, corresponding to them, to those of group IV:

Ga 69.9	Ge 72.3	As 75
In 113.7	Sn 118.1	Sb 120.3
Tl 204.1	Pb 206.91	Bi 208.

Their intermediate position accounts for their more non-metallic character. In this group, as in all other groups, it is noticed that as the atomic weight rises (from germanium to lead) there is a successive rise in metallo-basic character. All three members form dioxides,

GeO_2 SnO_2 PbO_2,

which may be viewed as anhydrides of the acids

GeO_3H_2 SnO_3H_2 PbO_3H_2.

These are perfectly analogous to silicic acid, but their stability and acidity diminish as the atomic weights of their basal elements increase.

Lead dioxide, PbO_2, combines with bases (especially the alkalies), forming salts of plumbic acid, *e.g.*, PbO_3K_2. These are not very stable; water decomposes them into their components. Lead dioxide does not unite with acids to yield salts. When digested with sulphuric acid it liberates an atom of oxygen, and forms salts of lead monoxide, PbO. It yields chlorine with hydrochloric acid. In this respect lead dioxide resembles the peroxides, *e.g.*, manganese peroxide, MnO_2, and is commonly known as lead peroxide. However, the salts, PbO_3Me_2, and the organo-metallic compounds, such as $Pb(CH_3)_4$, argue in favor of quadrivalent lead, and make it perfectly analogous to tin (pp. 268, 372).

The elements of this group yield monoxide derivatives,

GeO SnO PbO.

These are commonly known as *ous* compounds. They are basic and only form salts with acids. The basicity and stability of their derivatives increase as the atomic weights rise. The german*ous* and stann*ous* compounds are readily oxidized to derivatives of the dioxide type, while lead monoxide, PbO, is a strong base, and forms very stable salts. Compare p. 255 upon their behavior with metallic magnesium.

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1. GERMANIUM.

Ge = 72 3.

This element was discovered in 1886 by Cl. Winkler, of Freiberg. As early as 1871 Mendelejeff, with the periodic system as his basis, predicted the existence of an element with an atomic weight of about 73, which corresponded to the then existing gap between silicon and tin; he called it *ekasilicon* (the first analogue of silicon). The perfect agreement of the essential properties of germanium with those of the theoretical ekasilicon constitutes a brilliant confirmation of the law of periodicity (p. 360).

Winkler discovered germanium in the very rare mineral, argyrodite. The latter is a double sulphide of germanium and silver, $GeS_2.3Ag_2S$. It is also present in minute quantities in euxenite (together with titanium and zirconium) (Krüss). It may be separated from these minerals by fusing them with sulphur and soda. Sodium sulpho-germanate is then produced, and it is soluble in water (p. 367).

To obtain free germanium, its dioxide is heated in a current of hydrogen or reduced with carbon. The product is a dark-gray powder, which melts at 900°, and upon solidifying readily crystallizes into beautiful, grayish white, metallic octahedra. Its specific gravity at 20° equals 5.469. Its specific heat was found equal to 0.0737 at 100°, and at 440°, 0.0757. Therefore, its atomic heat at 100° is 5.33 and at 440°, 5.47. It increases very slightly with rise of temperature and is a little less than the mean atomic heat (p. 262).

Germanium is very stable in the air. When ignited it burns with the production of white vapors of germanium dioxide, GeO_2. The metal (like silicon) is insoluble in hydrochloric acid. Nitric acid converts it (like tin) into the hydrate of the dioxide. It is soluble in alkalies upon fusion. If it be heated in the gas flame, germanium will not impart a color to the same, and it does not show a spectrum. The latter can only be produced by the action of the induction spark.

Germanium, like tin, forms derivatives of the oxides GeO and GeO_2; the first are called german*ous* compounds, the latter german*ic*, or derivatives of germanic acid.

GERMANOUS COMPOUNDS.

These are not very stable, and are readily oxidized to the higher form.

Germanous Oxide—GeO—is formed when the hydroxide is ignited in a current of carbon dioxide. It is a grayish-black powder. **Germanous Hydroxide**—$Ge(OH)_2$—is precipitated as a yellow-colored compound upon the addition of caustic alkali to the solution of the chloride. It is soluble in hydrochloric acid.

Germanous Chloride—$GeCl_2$—has not been obtained pure. It is formed when hydrochloric acid gas acts upon heated germanous sulphide.

Germanous Sulphide—GeS—is a reddish-brown precipitate produced by the action of hydrogen sulphide upon the solution of the dichloride. It may be obtained in grayish-black crystals by heating germanium sulphide in hydrogen gas. It is soluble in hot hydrochloric acid, forming the corresponding chloride.

GERMANIC COMPOUNDS.

Germanium Tetrachloride—$GeCl_4$—is formed by the direct union of germanium with an excess of chlorine. The metal, when gently heated, burns in an atmosphere of chlorine, with a bluish color. When in powder form it inflames at the ordinary temperature. The tetrachloride is also produced if the sulphide, GeS_2, be heated together with mercuric chloride. It is a colorless, mobile liquid, of specific gravity 1.887 at 18°. It boils at 86°. It fumes strongly in the air, and is decomposed by water into hydrochloric acid and germanium hydroxide, $Ge(OH)_4$. Its vapor density, from 300–740°, equals 7.4 (air = 1), or 106.5 (H = 1), corresponding to the molecular formula, $GeCl_4 = 213.8$.

Germanium Chloroform—$GeHCl_3$—corresponding to ordinary chloroform, $CHCl_3$ (see p. 161), is produced when metallic germanium is heated in a current of hydrochloric acid gas. It is a mobile liquid, boiling about 72°. Its vapor density approximates the molecular formula $GeHCl_3$. It becomes cloudy on exposure to the air, and colorless, oily drops of **Germanium Oxychloride**, $GeOCl_2$ (?), separate.

Germanium Bromide—$GeBr_4$—is a strongly fuming liquid, which solidifies at 0° to a crystalline mass.

Germanium Iodide—GeI_4—results upon heating germanium chloride with potassium iodide, or more readily by conducting iodine vapor over heated and finely divided metal. It is an orange-colored solid, melting at 144°, and boiling at 400°.

Germanium Dioxide—GeO_2—germanic anhydride, is formed upon roasting the metal or the disulphide, or by treating the latter with nitric acid. It is a stable, white powder, of specific gravity

4.703 at 18°. It is slightly soluble in water (1 part in 95 parts at 100°) and imparts to the latter an acid reaction. **Germanic Hydroxide**, $Ge(OH)_4$, or $GeO(OH)_2$, **Germanic Acid**, is produced by directly transposing the chloride with water. It has not been obtained perfectly pure, as it loses more or less water. Like silicic acid, it is wholly acid in its character, and only forms salts with bases. It is soluble in the hydroxides and carbonates of the alkalies, especially on fusion, while it is almost insoluble in acids.

Germanic Sulphide—GeS_2.—Concentrated hydrochloric acid or sulphuric acid will precipitate it from solutions of its sulpho-salts. It is also formed when hydrogen sulphide is conducted through strongly acidulated solutions of the oxide. It is a white, voluminous precipitate, insoluble in acids, but readily soluble in water. If the precipitate is washed with water it dissolves. It is reprecipitated by acids, especially if hydrogen sulphide be conducted through the solution. The sulphide dissolves readily in the fixed alkaline hydroxides and ammonia. It forms *sulpho*-salts with the alkaline sulphides. These are perfectly analogous to the sulpho-stannates. Argyrodite is an example of this class (p. 365).

2. TIN.

$Sn = 118.1.$

Tin occurs in nature principally as dioxide (Cassiterite—tin stone) in England (Cornwall), Saxony, and India. To prepare the metal the oxide is roasted, lixiviated, and heated in a furnace with charcoal :—

$$SnO_2 + 2C = Sn + 2CO.$$

Thus obtained, it usually contains iron, arsenic, and other metals; to purify it the metal is fused at a low temperature, when the pure tin flows away, leaving the other metals. The tin obtained in the Indian isles (Malacca) is almost chemically pure, while that of England contains traces of arsenic and copper.

Tin is an almost silver-white, strongly lustrous metal, with a specific gravity of 7.3. It possesses a crystalline structure; and when a rod of it is bent it emits a peculiar sound (tin cry), due to the friction of the crystals. Upon etching a smooth surface of tin with hydrochloric acid, its crystalline structure is recognized by the appearance of remarkable striations. At low temperatures perfectly pure compact tin passes gradually into an aggregate of small quadratic crystals. The metal is tolerably soft, and very ductile, and may be rolled out into thin leaves. It becomes brittle at 200°, and may then be powdered. It fuses at 228°, and distils at a white heat (about 1700°); it burns with an intense white light when heated in the air, and forms tin dioxide. It does not oxidize in the air at ordinary temperatures, and withstands the action of many bodies, hence is employed in tinning copper and iron vessels for household use.

The most interesting of the tin alloys, besides bronze and soft solder, is britannia metal. It contains 9 parts tin and 1 part antimony, and frequently, also 2–3 per cent. zinc and 1 per cent. copper.

Tin dissolves in hot hydrochloric acid, to stannous chloride, with evolution of hydrogen gas:—

$$Sn + 2HCl = SnCl_2 + 2H.$$

Concentrated sulphuric acid, when heated, dissolves tin, with formation of stannous sulphate.

Somewhat dilute nitric acid oxidizes it to metastannic acid; while anhydrous nitric acid, HNO_3, does not change it. It dissolves when boiled with potassium or sodium hydroxides, forming stannates:—

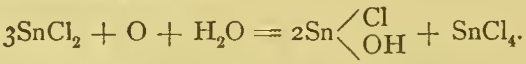
$$Sn + 2KOH + H_2O = SnO_3K_2 + 2H_2.$$

There are two series of compounds: the stannous, and stannic or compounds of stannic acid (p. 364).

STANNOUS COMPOUNDS.

Tin Dichloride—*Stannous chloride*, $SnCl_2$—results when tin dissolves in concentrated hydrochloric acid. When its solution is evaporated it crystallizes with two molecules of water ($SnCl_2 + 2H_2O$), which it loses at 100° C. It is used in dyeing, as a mordant, under the name of *Tin Salt*. The anhydrous chloride, obtained by heating the metal in dry hydrochloric acid gas, fuses at 250° and distils without decomposition at 606°. Its vapor density at 600–700° agrees with the formula Sn_2Cl_4; at 900° with $SnCl_2$.

Stannous chloride dissolves readily in water. Its solution is strongly reducing, and absorbs oxygen from air with the separation of basic stannous chloride:—



$$3SnCl_2 + O + H_2O = 2Sn\begin{cases}Cl\\OH\end{cases} + SnCl_4.$$

In the presence of hydrochloric acid, only stannic chloride is produced. Stannous chloride precipitates mercurous chloride and metallic mercury from solutions of mercuric chloride (p. 329). It unites with chlorine to form stannic chloride, and with many chlorides to yield double salts, *e. g.*:—

$$SnCl_2.2KCl \text{ and } SnCl_2.2NH_4Cl.$$

Tin Monoxide—SnO, or *Stannous oxide*—is obtained by heating its hydroxide, SnO_2H_2, in an atmosphere of carbon dioxide; it is a blackish-brown powder, which burns when heated in the air, and becomes stannic oxide. Sodium carbonate added to a solution of stannous chloride precipitates white

Stannous Hydroxide—*stanno-hydrate*—$Sn(OH)_2$:—

$$SnCl_2 + CO_3Na_2 + H_2O = Sn(OH)_2 + 2NaCl + CO_2.$$

It is insoluble in ammonium hydroxide, but is readily dissolved by potassium hydroxide. Upon slow evaporation of the alkaline solution, dark crystals of SnO separate; but, on boiling the solution, the hydrate decomposes into potassium stannate, K_2SnO_3, which remains dissolved, and metallic tin.

The hydroxide affords salts by its solution in acids. *Stannous chloride*—$SnCl_2$—and *stanno-sulphate*—$SnSO_4$—are formed when tin is warmed with concentrated hydrochloric or sulphuric acid. The sulphate separates in small, granular crystals, when its solution is evaporated.

Tin Monosulphide—*Stannous sulphide*—SnS—is precipitated from stannous solutions by hydrogen sulphide, as a dark-brown amorphous precipitate. Obtained by fusing tin and sulphur together, it is a lead-gray crystalline mass. It dissolves in concentrated hydrochloric acid, with liberation of H_2S, and forms stannous chloride. It is insoluble in alkaline sulphides, but, if sulphur be added and the solution boiled, it will dissolve as a sulpho-stannate (p. 370):—

$$SnS + S + K_2S = K_2SnS_3.$$

STANNIC COMPOUNDS.

Tin Tetrachloride—*Stannic chloride*—$SnCl_4$—is produced by the action of chlorine upon heated tin or stannous chloride—$SnCl_2$. It is a colorless liquid (*Spiritus fumans Libavii*), fuming strongly in moist air, of specific gravity 2.27, and boiling at 114°; its vapor density equals 129 ($H = 1$), corresponding to the molecular formula, $SnCl_4 = 258.9$. It attracts moisture from the air and is converted into a crystalline mass (Butter of Tin), $SnCl_4 + 3H_2O$, readily soluble in water. Boiling decomposes the solution into metastannic acid (H_2SnO_3) and hydrochloric acid:—

$$SnCl_4 + 3H_2O = H_2SnO_3 + 4HCl.$$

Stannic chloride possesses a salt-like nature, and combines with metallic chlorides to the so-called double salts, *e. g.*, $SnCl_4.2KCl$ and $SnCl_4.2NH_4Cl$; the latter compound is known as *pink salt* in calico printing. It also yields crystalline double salts with chlorides of the metalloids, *e. g.*, $SnCl_4.PCl_5$ and $SnCl_4.2SCl_4$.

Tin tetrachloride combines with hydrochloric acid, forming $SnCl_6H_2.6H_2O$, analogous to the chlorplatinate, $PtCl_6H_2.6H_2O$. It is formed when hydrochloric acid gas is conducted into a concentrated solution of tin tetrachloride in water. In the cold it solidifies to a leafy crystalline mass, melting at + 9°.

Tin Bromide—$SnBr_4$—forms a white, crystalline mass that melts at 30° and boils at 200°. It unites with hydrogen bromide, forming $SnBr_6H_2.7H_2O$, crystallizing in yellow needles and plates.

Tin Iodide—SnI_4—consists of orange-red octahedra, fusing at 146° and boiling at 295°. It may be obtained by heating tin with iodine to 50°.

Tin Fluoride—$SnFl_4$—is only known in combination with metallic fluorides (*e.g.*, K_2SnFl_6), which are very similar to and generally isomorphous with the salts of hydrofluosilicic acid ($SiFl_6K_2$).

Tin Dioxide—*Stannic oxide*—SnO_2—is found in nature as tin stone, in quadratic crystals or thick brown masses, of specific gravity 6.8. It is prepared, artificially, by heating tin in the air, and it then forms a white amorphous powder. It may be obtained crystallized, by conducting vapors of the tetrachloride and water through a tube heated to redness. The dioxide is infusible, and not soluble in acids or alkalies. When fused with sodium and potassium hydroxide it yields stannates soluble in water.

On adding ammonium hydroxide to the aqueous solution of tin tetrachloride or hydrochloric acid to the solution of potassium stannate (SnO_3K_2), a white precipitate of *stannic acid* will separate. This dissolves readily in concentrated nitric acid, hydrochloric acid and the alkalies. If preserved under water, or *in vacuo*, it becomes insoluble in acids and sodium hydroxide. Both modifications appear to have the same composition, H_2SnO_3, and the cause of the isomerism is not yet explained. The insoluble modification is commonly called *metastannic acid*. It is also obtained as a white powder by digesting tin with dilute nitric acid. On adding sodium hydroxide to the insoluble stannic acid it is converted into sodium metastannate, insoluble in sodium hydroxide, but readily dissolved by pure water. The salts of stannic oxide with acids, *e. g.*, the sulphate, are not very stable, and washing with warm water decomposes them. The metal salts of stannic acid are more stable. The most important of these is *sodium stannate*—$Na_2SnO_3 + 3H_2O$—which is employed in calico printing, under the name of *preparing salts*. It is produced upon a large scale by fusing tin stone with sodium hydroxide. On evaporating the solution, it crystallizes in large, transparent, hexagonal crystals, containing three molecules of water.

Tin Disulphide—*Stannic sulphide*—SnS_2—is precipitated as an amorphous, yellow powder by H_2S from stannic solutions. If a mixture of tin-filings, sulphur, and ammonium chloride be heated it is obtained in form of a brilliant crystalline mass, consisting of gold-yellow scales. It is then called *mosaic gold*, and is applied in bronzing. Concentrated hydrochloric acid dissolves the precipitated disulphide, forming stannic chloride; nitric acid converts it into metastannic acid. The sulphides and hydrosulphides of the alkalies dissolve tin disulphide forming sulphostannates (see p. 226). *Sodium sulphostannate*, $SnS_3Na_2 + 2H_2O$, crystallizes in colorless octahedra. Acids decompose the sulphostannates with the separation of tin disulphide.

3. LEAD.

$Pb = 206.91$.

Lead (*Plumbum*) is found in nature principally as *Galenite*—PbS. The other more widely distributed lead ores are *Cerussite*—$PbCO_3$—*Crocoisite* ($PbCrO_4$) and *Wulfenite* (MoO_4Pb). Galenite is the chief source of lead; the process of its separation is very simple. The galenite is first roasted in the air and then strongly ignited away from it. In the roasting, a portion of the lead sulphide is oxidized to oxide and sulphate:—

$$PbS + 3O = PbO + SO_2$$

and

$$PbS + O_4 = PbSO_4.$$

Upon ignition, these two substances react with the lead sulphide according to the following equations:—

$$2PbO + PbS = 3Pb + SO_2$$

and

$$SO_4Pb + PbS = 2Pb + 2SO_2.$$

Metallic lead has a bluish-white color, is very soft, and tolerably ductile. A freshly cut surface has a bright lustre, but on exposure to air becomes dull by oxidation. Its specific gravity is 11.37. It fuses at 325°, and distils at a white heat (about 1700°). It burns to lead oxide when heated in the air.

In contact with air and water lead oxidizes to lead hydroxide, $Pb(OH)_2$, which is somewhat soluble in water. If, however, the water contain carbonic acid and mineral salts—even in slight quantity, as in natural waters—no lead goes into solution, but it is covered with an insoluble layer of lead carbonate and sulphate. When much carbon dioxide is present the carbonate is somewhat soluble in the water. This behavior is very important for practical purposes, as lead pipes are frequently employed in conducting water.

Sulphuric and hydrochloric acid have little effect on the metal, owing to the insolubility of its sulphate and chloride; yet, if the lead be in the form of powder, both acids will dissolve it. It forms lead nitrate with dilute nitric acid. Zinc, tin, and iron precipitate it, as metal, from its solution; a strip of zinc immersed in a dilute solution of lead acetate is covered with an arborescent mass, consisting of shining crystalline leaflets (lead tree).

Alloys.—An alloy of equal parts lead and tin fuses at 186°, and is used for soldering (soft solder). An alloy of 4–5 parts of lead and 1 part of antimony is very hard, and answers for the manufacture of type (hard lead or type-metal).

The usual lead compounds are constituted according to the type PbX_2, and are called *plumbic* (p. 364). They show a slight similarity to the stannous derivatives. Many of the lead salts are isomorphous with those of barium; the sulphates of both metals are insoluble.

The heat of formation of some of the lead compounds equals:—

$$(Pb,Cl_2) = 82.7 \quad (Pb,Br_2) = 64.4 \quad (Pb,I_2) = 39.6 \quad (Pb,O) = 50.3.$$
$$(PbO,O) = 12.1 \quad (Pb,S) = 20.4 \quad (Pb,S,O_4) = 216.2 \quad (Pb,N_2,O_6) = 105.5.$$

If we include the heat of solution with the above numbers, they will afford us an explanation for the deportment of lead toward acids, as well as for the various transpositions of its compounds.

The heats of formation of the corresponding tin compounds are as follows:—

$$(Sn,Cl_2) = 80.8 \qquad (Sn,Cl_4) = 127$$
$$(Sn,O) = 68 \qquad (Sn,O_2) = 136.$$

Compared with the lead derivatives, it is evident from these figures that tin will separate lead from the plumbates, while tin is usually precipitated from its salts by lead.

Lead Oxide—PbO—is produced when lead is heated in air. After fusion it solidifies to a reddish-yellow mass of rhombic scales (litharge). When lead is carefully roasted, or the hydroxide or nitrate ignited, we obtain a yellow amorphous powder called massicot. Lead oxide has strong basic properties; it absorbs carbon dioxide from the air, and imparts an alkaline reaction to water as it dissolves as hydroxide. Like other strong bases it saponifies fats. It dissolves in hot potassium hydroxide, and on cooling crystallizes from solution in rhombic prisms.

Lead Hydroxide—$Pb(OH)_2$.—Alkalies throw it out of lead solutions as a white, voluminous precipitate.

It imparts an alkaline reaction to water, as it is somewhat soluble, and absorbs carbon dioxide with formation of lead carbonate. When heated to 130° it decomposes into lead oxide and water.

If lead or the amorphous oxide be heated to 300–400°, for some time, in the air, it will absorb oxygen and be converted into a bright-red powder, called *red lead*, or minium. Its composition corresponds to the formula, Pb_3O_4; it is considered a compound of PbO with lead peroxide ($Pb_3O_4 = 2PbO + PbO_2$). When minium is treated with somewhat dilute nitric acid, lead nitrate passes into solution, while a dark-brown amorphous powder—**lead peroxide**, PbO_2—remains.

This oxide is more conveniently obtained by adding bleaching lime (and milk of lime) to a concentrated lead chloride solution (in calcium chloride):—

$$2PbCl_2 + Ca(OCl)_2 + 2H_2O = 2PbO_2 + CaCl_2 + 4HCl.$$

Or chlorine is conducted into a mixture of lead chloride (2 mols.) and calcium hydroxide (3 mols.) with water.

Lead peroxide dissolves in cold hydrochloric acid to a reddish-yellow liquid containing *lead tetrachloride*, $PbCl_4$. The latter also results from the action of chlorine gas on a mixture of lead chloride with hydrochloric acid. The tetrachloride cannot be obtained free, because its solution readily decomposes into $PbCl_2$ and chlorine.

Oxygen is disengaged when sulphuric acid acts upon it, and lead sulphate ($PbSO_4$) formed. When dry sulphur dioxide is conducted over it, glowing sets in and lead sulphate results:—

$$PbO_2 + SO_2 = PbSO_4.$$

When ignited PbO_2 breaks up into PbO and oxygen.

As previously mentioned (p. 364), lead dioxide, like that of tin, has an acid nature. When warmed with potassium hydroxide, it dissolves, and on cooling, large crystals of *potassium plumbate*—$K_2PbO_3 + 3H_2O$—separate out; these are perfectly analogous to potassium stannate—$K_2SnO_3 + 3H_2O$. An alkaline lead oxide solution added to a solution of potassium plumbate produces a yellow precipitate ($Pb_3O_4 + H_2O$), which loses water upon gentle warming, and is converted into *red lead*. Therefore, the latter must be considered as the lead salt of a normal plumbic acid, $Pb(OH)_4$, which corresponds to stannic, $Sn(OH)_4$, and silicic, $Si(OH)_4$, acids:—

$$Pb_3O_4 = Pb_2PbO_4.$$

Another oxide—Pb_2O_3—which is precipitated as a reddish-yellow powder on the addition of sodium hypochlorite to an alkaline lead solution, is very probably the lead salt of metaplumbic acid: $Pb_2O_3 = PbPbO_3$. Nitric acid decomposes it into lead nitrate and peroxide. It dissolves in hydrochloric acid without liberation of chlorine; this gas escapes, however, when the solution is heated.

Lead Chloride—$PbCl_2$—separates as a white precipitate, when hydrochloric acid is added to the solution of a lead salt. It is almost insoluble in cold water; from hot water, of which it requires 30 parts for solution, it crystallizes in white, shining needles. It melts about 500° and solidifies to a horn-like mass. It is volatile at a white heat; its vapor density corresponds to the formula $PbCl_2$.

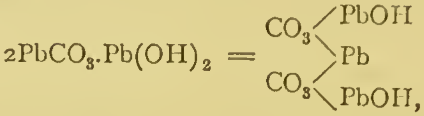
Lead Iodide—PbI_2—is thrown down as a yellow precipitate from lead solutions by potassium iodide; it crystallizes from a hot solution in shining, yellow leaflets, melting at 383°.

Lead Nitrate—$Pb(NO_3)_2$—obtained by the solution of lead in nitric acid, crystallizes in regular octahedra (isomorphous with barium nitrate) and dissolves in 8 parts water. It melts at a red heat, and is decomposed into PbO, NO_2 and oxygen. When boiled with lead oxide and water, it is converted into the basic nitrate, $Pb\begin{smallmatrix}\diagup NO_3 \\ \diagdown OH\end{smallmatrix}$, which separates in white needles.

Lead Sulphate—$PbSO_4$—occurs in nature as *Anglesite*, in rhombic crystals, isomorphous with barium sulphate. It is precipitated from lead solutions as a white crystalline mass by sulphuric acid. It dissolves with difficulty in water, more readily in concentrated sulphuric acid. When ignited with carbon, it is decomposed according to the following equation:—

$$PbSO_4 + 2C = PbS + 2CO_2.$$

Lead Carbonate—$PbCO_3$—occurs as *Cerussite* in nature. It is precipitated by ammonium carbonate from lead nitrate solutions. Potassium and sodium carbonates precipitate basic carbonates, the composition of which varies with the temperature and concentration of the solution. A similar basic salt, whose composition agrees best with the formula:—



$$2PbCO_3.Pb(OH)_2 = \begin{array}{ll} CO_3 & \diagup PbOH \\ & \diagdown \\ & \quad Pb \\ & \diagup \\ CO_3 & \diagdown PbOH, \end{array}$$

is prepared on a large scale by the action of carbon dioxide upon lead acetate. It bears the name of *white lead.*

White lead was formerly manufactured by what is known as the Dutch process. Rolled lead sheets were moistened in earthenware pots, with acetic acid, and then covered with manure and permitted to stand undisturbed for some time. In this way, the action of the acetic acid and air upon the lead produced a basic acetate, which the CO_2, evolved from the decaying manure, converted into basic lead carbonate. At present it is prepared by dissolving litharge in acetic acid, and converting the resulting basic acetate into a carbonate by conducting carbon dioxide into it.

White lead is employed for the manufacture of white oil colors. As it is poisonous, and blackened by the hydrogen sulphide of the air (formation of lead sulphide), it is being replaced more and more by zinc white and permanent white ($BaSO_4$).

Lead Sulphide—PbS—occurs crystallized in metallic, shining cubes and octahedra. Hydrogen sulphide precipitates it as an amorphous black powder. It is insoluble in dilute acids.

The lead compounds are very poisonous. The soluble salts have a sweetish, astringent taste. They are readily recognized by the following reactions: sulphuric acid precipitates white lead sulphate, which is blackened by hydrogen sulphide; potassium iodide precipitates yellow lead iodide.

BISMUTH.

Bi = 208.

Bismuth constitutes a natural group with antimony, arsenic, phosphorus and nitrogen, and, like these, affords compounds of the forms BiX_3 and BiX_5. We observed that, with increase of atomic weight, the metalloidal character of the lower members becomes more metallic (see p. 150); the acid nature of the oxides passes into a basic. Antimony oxide (Sb_2O_3) is a base, while the higher oxide, Sb_2O_5, represents an acid anhydride. In bismuth, the metallic nature attains its full value. This is manifest in its inability to unite with hydrogen. Bismuth trioxide is a base, and the pentoxide possesses a very feeble acid character, yielding indefinite compounds with the alkalies; it behaves more like a metallic peroxide, and in its properties exhibits great similarity to lead peroxide.

Bismuth usually occurs native, and in combination with sulphur, as bismuthinite. To obtain the metal, the sulphide is roasted in the air, and the resulting oxide reduced with charcoal.

Bismuth is a reddish-white metal, of specific gravity 9.9. It is brittle and may be easily pulverized. It crystallizes in rhombohedra. It fuses at 267° and distils at a white heat (about 1300°). It does not change in the air at ordinary temperatures. When heated it burns to bismuth oxide—Bi_2O_3. It is insoluble in hydrochloric acid, but dissolves in boiling sulphuric acid with formation of sulphate of bismuth, and the evolution of sulphur dioxide. Nitric acid dissolves it readily in the cold.

Water decomposes bismuth solutions in the same manner as those of antimony; insoluble basic salts are precipitated, but these are not dissolved by tartaric acid.

Bismuthous Chloride—$BiCl_3$—arises from the action of chlorine upon heated bismuth, and by the solution of the metal in aqua regia. It is a soft white mass which fuses at 230° and boils about 435°. It deliquesces in the air. Water renders its solution turbid, a white, crystalline precipitate of *Bismuth Oxychloride*—$BiOCl$—separating at the same time:—

$$BiCl_3 + H_2O = BiOCl + 2HCl.$$

The metalloidal character of bismuth is indicated by this reaction.

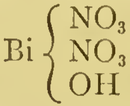
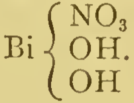
The compounds $BiBr_3$ and BiI_3 are very similar to bismuth chloride. All three combine with many metallic haloid salts to form double halogen derivatives.

Halogen derivatives of pentavalent bismuth are unknown.

Bismuth Oxide—Bi_2O_3—prepared by burning bismuth or heating the nitrate, is a yellow powder, insoluble in water and the alkalies.

Normal **bismuth hydroxide**—$Bi(OH)_3$—is not known in a free state. Potassium hydroxide added to a bismuth solution precipitates a white amorphous *metahydrate*—$BiO.OH$.

Chlorine conducted through a concentrated potassium hydroxide solution in which bismuth oxide is suspended precipitates red **bismuthic acid** (BiO_3H or $Bi_2H_4O_7$), which when gently heated becomes Bi_2O_5, *bismuthic oxide.* Strong ignition converts the latter into Bi_2O_3 and O_2; hydrochloric acid dissolves it to bismuth chloride, with liberation of chlorine.

Bismuth Nitrate—$Bi(NO_3)_3$—is obtained by the solution of bismuth in nitric acid, and crystallizes with 5 molecules of H_2O in large, transparent tables. In a little water it dissolves without any change; much water renders it turbid, owing to the precipitation of white, curdy basic salts:  $Bi\left\{\begin{matrix}NO_3\\NO_3\\OH\end{matrix}\right.$ and  $Bi\left\{\begin{matrix}NO_3\\OH\\OH\end{matrix}\right.$. The precipitate is employed in medicine under the name of *Magisterium bismuthi* (*subnitrate*).

Bismuth Sulphate—$Bi_2(SO_4)_3$—is formed when bismuth dissolves in sulphuric acid. It crystallizes in delicate needles. **Bismuth Sulphide**—Bi_2S_3—occurring as bismuthinite, is thrown down as a black precipitate from bismuth solutions by hydrogen sulphide. Unlike antimony and arsenic sulphides, it does not form sulpho-salts.

The **alloys** of bismuth are nearly all readily fusible. An alloy of 4 parts Bi, 1 part Cd, 1 part Sn and 2 parts Pb, fuses at 65° (Wood's metal). The alloy of 2 parts bismuth, 1 part lead and 1 part tin (Rose's metal) fuses at 94°.

CHROMIUM GROUP.

We observed that a group of more metallic analogous elements attached itself to the metalloidal elements, carbon, silicon and tin (p. 241); and further that there was an analogous group of metallic elements corresponding to the metalloidal group of phosphorus (p. 229). We now meet a group of metals, consisting of chromium, molybdenum, tungsten, and probably uranium, that bears a like relation to the elements of the sulphur group (see Periodic System of the Elements). The resemblance of these elements to sulphur and its analogues is plainly manifest in their highest oxygen derivatives (see also manganese). As the elements of the sulphur group in their highest oxygen compounds are hexavalent, so chromium, molybdenum, tungsten and uranium form acid oxides—CrO_3, MoO_3, WO_3, UrO_3. Many of the salts corresponding to these are very similar to and isomorphous with the salts of sulphuric acid. Sodium chromate, like sodium sulphate, crystallizes with 10 molecules of water; the potassium salts of both groups form isomorphous mixtures; their magnesium salts, as well as that of tungstic acid, have the same constitution:—

$$MgSO_4 + 7H_2O \text{ and } MgCrO_4 + 7H_2O.$$

Corresponding to the acid oxides are the chlorine derivatives:—

$$SO_2Cl_2,\ CrO_2Cl_2,\ MoO_2Cl_2,\ MoOCl_4,\ WOCl_4 \text{ and } WCl_6,$$

which are perfectly analogous, so far as chemical deportment is concerned. Besides these highest oxides the elements of the sulphur group form the less acid oxides:—

$$\overset{IV}{SO_2},\quad \overset{IV}{SeO_2}\quad \text{and}\quad \overset{IV}{TeO_2}.$$

Of these the last approaches the bases. Their analogues in the chromium group: CrO_2, MoO_2, WO_2, in which the elements appear tetravalent, possess an undetermined, neither acid nor basic, character.

The most important basic oxide of chromium is its sesquioxide. This affords salts with the acids, and they are perfectly similar to those of the sesquioxides of iron (Fe_2O_3), manganese (Mn_2O_3), and aluminium (Al_2O_3) (p. 334).

Since the vapor density of ferric chloride declares its formula to be Fe_2Cl_6, we assume that in their sesquioxide compounds Cr, Mn, and Fe are tetravalent, and that these contain a hexavalent group consisting of two atoms of metal:—

$$\equiv\overset{IV}{Cr} - \overset{IV}{Cr}\equiv \qquad\qquad Cl_3\overset{IV}{Cr} - \overset{IV}{Cr}Cl_3, \text{ etc.}$$

We can, however, conceive these derivatives, as well as those of aluminium, as derived from trivalent metallic atoms, and then make use of the simple, instead of the double formulas (CrX_3 and FeX_3). (Compare pp. 343 and 350.) These facts are confirmed by the most recent determinations of the vapor density of aluminium, ferric and chromic chlorides, which accords with the formulas $AlCl_3$, $FeCl_3$, and $CrCl_3$ (p. 378).

Finally, compounds of chromium, $\overset{II}{Cr}X_2$, are known in which the metal figures as a dyad. These so-called *chromous* compounds are very much like (p. 333) the derivatives of the metals of the magnesium group, especially the ferrous salts (FeX_2). They are very unstable, and are oxidized by the air into chromic compounds.

Salts of molybdenum and tungsten, corresponding to the states of lowest oxidation, are not known, because these metals occur as hexads in most of their derivatives. Uranium, which has the highest atomic weight of the group, shows some variations from its analogues; these are explained, as in similar cases, by its high atomic weight.

1. CHROMIUM.

$Cr = 52.2.$

Chromium is found principally as chromite in nature. This is a combination of chromic oxide with ferrous oxide—Cr_2O_3FeO—and occurs in North America, Sweden, Hungary, and in large quantities in the Urals. Crocoisite, or lead chromate ($PbCrO_4$), is not met with so frequently. Chromic iron is used almost exclusively for the preparation of all other chromium derivatives, as it is first converted into potassium chromate (see this) by fusion with potassium carbonate and nitrate.

Metallic chromium may be isolated by the very strong ignition of the oxide with charcoal. It is more conveniently obtained by igniting a mixture of chromium chloride, potassium chloride or sodium chloride with zinc, in a closed crucible. The separated chromium dissolves in the molten zinc, and when the latter is dissolved in nitric acid the chromium remains behind as a gray, metallic, crystalline powder, of specific gravity 6.8. It is very hard (cuts glass), and fuses with difficulty. When heated in the air it slowly oxidizes to chromic oxide; ignited in oxygen it burns with a bright light. It dissolves readily in hydrochloric and warm dilute sulphuric acid, with elimination of hydrogen; it is not altered by nitric acid.

Three series of chromium compounds are known: *chromous*—CrX_2, *chromic*—Cr_2X_6, and the derivatives of chromic acid, called *chromates*. All chromium compounds are brightly colored, hence, the name chromium (from χρῶμα, color).

CHROMOUS COMPOUNDS.

These are very unstable, and by oxidation pass readily into *ic* compounds. Like ferrous salts, they are produced by the reduction of the higher oxides. The following may be mentioned: **Chromous Chloride**, $CrCl_2$. This is obtained by heating chromic chloride, Cr_2Cl_6, in a stream of hydrogen. It is a white crystalline powder. It volatilizes without decomposition. At 1300–1600° the vapor density corresponds to a mixture of the molecules $CrCl_2$ and Cr_2Cl_4. It dissolves in water with a blue color; the solution absorbs oxygen with avidity, and becomes green in color. The alkalies precipitate yellow **chromous hydroxide**, $Cr(OH)_2$, from it. This is readily oxidized. When heated it parts with hydrogen and water and becomes chromic oxide: $2Cr(OH)_2 = Cr_2O_3 + H_2 + H_2O$.

CHROMIC COMPOUNDS.

Chromic Chloride—Cr_2Cl_6, like Al_2Cl_6—is obtained by ignition of the oxide and charcoal in a current of chlorine. When raised to a red heat in this condition it sublimes in shining violet leaflets, which are transformed into chromic oxide by ignition in the air. Its vapor density at 1200–1300° corresponds to the formula $CrCl_3$; it vaporizes very slowly below 1000°. Pure chromic chloride only dissolves in water after long-continued boiling; if, however, it contains traces of $CrCl_2$, it dissolves readily at ordinary temperatures. Green crystals of $Cr_2Cl_6 + 12H_2O$ separate from the green solution on evaporation; these deliquesce in the air. The same crystals may be obtained from solutions of chromic hydroxide, $Cr_2(OH)_6$, in hydrochloric acid. When they are dried intermediate oxychlorides, $Cr_2Cl_4(OH)_2$, and $Cr_2Cl_2(OH)_4$, and at last $Cr_2(OH)_6$ result.

Chromic Hydroxide—$Cr_2(OH)_6$ or $Cr(OH)_3$.—It is precipitated by ammonium hydroxide from chromic solutions as a voluminous bright brown, hydrous mass. The green precipitates produced by sodium and potassium hydroxides, contain alkali that cannot be removed even by boiling water. They dissolve readily with an emerald green color, in an excess of KOH or NaOH (slightly in ammonia), but are reprecipitated upon boiling their solutions. When it is heated to 200° in a current of hydrogen, the product is the hydroxide, CrO.OH, which is a grayish-blue powder, insoluble in dilute hydrochloric acid. When chromium hydroxide is ignited, it becomes chromic oxide.

Chromic Oxide—Cr_2O_3—is a green, amorphous powder. It is also formed by the ignition of chromium trioxide:—

$$2CrO_3 = Cr_2O_3 + 3O,$$

or of ammonium bichromate:—

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + N_2.$$

It may be obtained in black, hexagonal crystals, by conducting the vapors of the oxychloride through a tube heated to redness:—

$$2CrO_2Cl_2 = Cr_2O_3 + 2Cl_2 + O.$$

Ignited chromic oxide is insoluble in acids. When fused with silicates, it colors them emerald green, and serves, therefore, to color glass and porcelain.

Guignet's green is a beautifully green-colored chromium hydroxide, which is applied as a paint. It is obtained by igniting a mixture of one part potassium bichromate with three parts boric acid; after treating the mass with water, which dissolves potassium borate, there remains a green powder, the composition of which corresponds to the formula:—

$$Cr_2O(OH)_4 = Cr_2O_3.2H_2O.$$

The predominating properties of chromic oxide are basic, as it readily affords salts with acids; yet its basic nature, like that of all sequioxides, is but slight, so that it does not afford salts with weak acids (p. 380). In addition to all this it possesses a slightly acidic character, and metallic salts are derived from it, generally from the hydroxide, CrO.OH, which are analogous to the aluminates (p. 354). Salts, like $(CrO.O)_2Mg$ and $(CrO.O)_2Zn$, can be obtained crystallized in regular octahedra by fusing chromic oxide with metallic oxides and boron trioxide (as flux). Chromic iron is such a salt:—

$$Cr_2O_3.FeO = (CrO.O)_2.Fe.$$

Chromium Sulphate—$Cr_2(SO_4)_3$—is obtained by dissolving the hydroxide in concentrated sulphuric acid. The solution, green at first, becomes violet on standing, and deposits a violet-colored crystalline mass. This may be purified by solution in water and precipitation by alcohol. This salt crystallizes from very dilute alcohol in bluish-violet octahedra containing 15 molecules of water. If the aqueous solution of the violet salt be heated, it assumes a green color, because the salt breaks up into free acid and a basic salt which, upon evaporation, separates as a green amorphous mass, soluble in alcohol. When the green solution stands, it reverts to the violet of the neutral salt. The other chromic salts, the nitrate and the alum, behave in a similar manner.

Chromium sulphate forms double salts with the alkaline sulphates—the chromium alums (p. 355).

Potassium Chromium Alum—$CrK(SO_4)_2 + 12H_2O$—crystallizes in large, dark violet octahedra. It may be most conveniently prepared by acting upon a solution of potassium bichromate mixed with sulphuric acid, with sulphur dioxide:—

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = Cr_2(SO_4)_3.K_2SO_4 + H_2O.$$

At 80° the violet solution of the salt becomes green, and on evaporation affords an amorphous green mass.

As chromium oxide possesses only a slightly basic nature, salts with weak acids, like CO_2, SO_2, H_2S (see Aluminium, p. 355) do not exist. Therefore, the alkaline carbonates and sulphides precipitate chromium hydroxide from solutions of chromium salts:—

$$Cr_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O = Cr_2(OH)_6 + 3Na_2SO_4 + 3CO_2$$

and

$$Cr_2(SO_4)_3 + 3(NH_4)_2S + 6H_2O = Cr_2(OH)_6 + 3(NH_4)_2SO_4 + 3H_2S.$$

Ammonium sulphide produces a black precipitate—CrS—in solutions of chromous salts.

DERIVATIVES OF CHROMIC ACID.

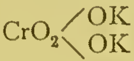
In its highest oxygen derivative, CrO_3, chromium possesses a complete metalloidal, acid-forming character. Chromic acid, H_2CrO_4, is perfectly analogous to sulphuric acid, H_2SO_4, but has not been obtained free, since when liberated from its salts it at once breaks up into the oxide and water:—

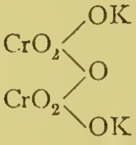
$$H_2CrO_4 = CrO_3 + H_2O.$$

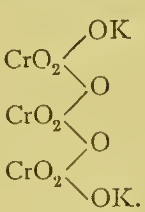
The chromates are often isomorphous with the sulphates (p. 376). *Polychromates* also exist, and are derived from polychromic acids produced by the condensation of several molecules of the normal acid (see Disulphuric acid, p. 197):—

K_2CrO_4,	$K_2Cr_2O_7$,	$K_2Cr_3O_{10}$, etc.
Potassium chromate.	Potassium bichromate.	Potassium trichromate.

The constitution of these salts is expressed by the following formulas:—







The free polychromic acids are not known, because as soon as they are separated from their salts, they immediately break up into the acid oxide and water:—

$$H_2Cr_3O_{10} = 3CrO_3 + H_2O.$$

The polychromates are frequently, but incorrectly, called acid salts; true acid or primary salts, in which only one H atom is replaced by metal (CrO_4KH), are unknown for chromic acid.

The salts of normal chromic acid are mostly yellow-colored, while the polychromates are red. The latter are produced from the former by the action of acids:—

$$2K_2CrO_4 + 2HNO_3 = K_2Cr_2O_7 + 2KNO_3 + H_2O.$$

Conversely, by the action of the alkalies, the polychromates pass into the normal salts:—

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O.$$

Their formation may also be as follows: The chromic acid liberated from its salts by stronger acids breaks up into water and the acid oxide, which combines with the excess of the normal chromate:—

$$CrO_4K_2 + CrO_3 = K_2Cr_2O_7.$$

When there is an excess of acid the anhydride (CrO_3) is set free.

Chromium Trioxide—*Chromic Acid Anhydride*—CrO_3.—It consists of long, red, rhombic needles or prisms, obtained by adding sulphuric acid to a concentrated potassium bichromate solution. The crystals deliquesce in the air and are readily soluble in water. When heated, they blacken, melt, and at about 250° decompose into chromic oxide and oxygen:—

$$2CrO_3 = Cr_2O_3 + 3O.$$

Chromium trioxide is a powerful oxidizing agent, and destroys organic matter; hence its solution cannot be filtered through paper. When alcohol is poured on the crystals, detonation takes place, the alcohol burns, and green chromic oxide remains. By the action of acids, *e.g.*, sulphuric, the trioxide deports itself like a peroxide; oxygen escapes and a chromic salt results. When heated with concentrated hydrochloric acid chlorine is evolved:—

$$2CrO_3 + 12HCl = Cr_2Cl_6 + 6H_2O + 3Cl_2.$$

Reducing substances, like sulphurous acid and hydrogen sulphide, convert chromic acid into oxide:—

$$2CrO_3 + 3H_2S = Cr_2O_3 + 3H_2O + 3S.$$
$$2CrO_3 + 3SO_2 + 3H_2O = Cr_2O_3 + 3SO_4H_2.$$

Chromate of Potassium—K_2CrO_4—is obtained by adding potassium hydroxide to potassium bichromate. It forms yellow rhombic crystals, isomorphous with potassium sulphate (K_2SO_4); isomorphous mixtures crystallize out from the solution of the two salts.

Bichromate of Potassium—$K_2Cr_2O_7$—called acid potassium chromate, is manufactured on a large scale, and bears the name *red chromate of potash* in commerce. It is obtained by igniting pulverized chromite, Cr_2O_3FeO, with potashes and nitre, whereby potassium chromate and ferric oxide are formed. The fusion is treated with water, and the resulting solution of potassium chromate, K_2CrO_4, mixed with acetic or nitric acid (see p. 381), when potassium bichromate crystallizes from the concentrated solution.

In practice the above method is advantageously replaced by the following: The pulverized chromite is ignited, together with lime, in furnaces allowing air access. Calcium chromate ($CaCrO_4$) (together with ferric oxide) is produced. This dissolves in dilute sulphuric acid to bichromate, $CaCr_2O_7$; the latter is converted by potassium carbonate into potassium bichromate.

Bichromate of potassium crystallizes in large, red, triclinic prisms, soluble at ordinary temperatures, in 10 parts of water. When heated, the salt fuses without change; at a very high heat it decomposes into potassium chromate, chromic oxide and oxygen:—

$$2K_2Cr_2O_7 = 2K_2CrO_4 + Cr_2O_3 + O_3.$$

When the salt is warmed with sulphuric acid, oxygen escapes and potassium chromium alum is produced:—

$$K_2Cr_2O_7 + 4H_2SO_4 = Cr_2(SO_4)_3.K_2SO_4 + 4H_2O + 3O.$$

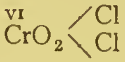
This reaction answers for the preparation of perfectly pure oxygen. Further, the mixture is made use of in laboratories, as an oxidizing agent.

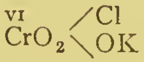
Chromate of Sodium—$Na_2CrO_4 + 10H_2O$—forms deliquescent crystals, and is analogous to Glauber's salt ($Na_2SO_4 + 10H_2O$). **Barium and Strontium Chromates**—$BaCrO_4$ and $SrCrO_4$—are almost insoluble in water. **Calcium Chromate**—$CaCrO_4$—dissolves with difficulty in water, and crystallizes like gypsum with two molecules of water. The *magnesium salt*, $MgCrO_4 + 7H_2O$, dissolves readily and corresponds to Epsom Salt. The chromates of the heavy metals are insoluble in water, and are obtained by transposition.

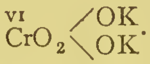
Chromate of Lead—$PbCrO_4$—is obtained by the precipitation of soluble lead salts with potassium chromate. It is a yellow amorphous powder which serves as a yellow paint. When heated it melts undecomposed, and solidifies to a brown, radiating crystalline mass. It oxidizes and easily decomposes all the carbon compounds, and is therefore used in their analysis. In nature lead chromate exists as crocoisite.

The oxide, CrO_2, called *peroxide*, may be obtained by the careful ignition of chromium trioxide, and is, most likely, a salt-like compound: $Cr_2O_3.CrO_3$ or $CrO.CrO_3$. Its hydrate is precipitated from chromium solutions upon the addition of potassium chromate. On warming the peroxide with hydrochloric acid, chlorine is evolved.

Chromic Acid Chloranhydrides.—Chromic acid forms chloranhydrides similar to those of sulphuric acid (p. 199). Corresponding to SO_2Cl_2, we have chromyl chloride, CrO_2Cl_2; and for the first sulphuric acid chloranhydride, $SO_2\begin{cases}Cl\\OH\end{cases}$, is the salt, $CrO_2\begin{cases}Cl\\OK\end{cases}$:—







Chromyl Chloride—CrO_2Cl_2—*Chromium oxychloride*, is produced by heating a mixture of potassium (or sodium) bichromate (or monochromate) and sodium chloride with sulphuric acid:—

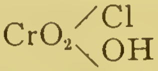
$$CrO_4Na_2 + 2NaCl + 2SO_4H_2 = CrO_2Cl_2 + 2SO_4Na_2 + 2H_2O,$$

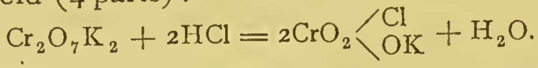
and

$$Cr_2O_7Na_2 + 4NaCl + 3SO_4H_2 = 2CrO_2Cl_2 + 3SO_4Na_2 + 3H_2O.$$

The water produced at the same time must be absorbed by the excess of sulphuric acid. To prepare chromyl chloride, first fuse salt (10 parts) with potassium dichromate (12 parts) or with potassium monochromate (17 parts). The yellowish-brown mass is broken into coarse pieces, placed into a retort provided with a condenser, and anhydrous or slightly fuming sulphuric acid (30 parts) poured over them. When a gentle heat is applied chromyl chloride distils over and is purified by further distillation. It is a red, transparent liquid, of specific gravity 1.92 at 25°, and fumes strongly in the air. It boils at 116°–118°; its vapor density equals 77 ($H = 1$), corresponding to the molecular formula $CrO_2Cl_2 = 154$. Chromyl chloride has a strong oxidizing action. With water it is decomposed according to the following equation:—

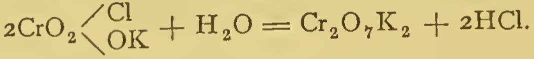
$$CrO_2Cl_2 + H_2O = CrO_3 + 2HCl.$$

Chloro-chromic Acid,  $CrO_2\Big\langle\begin{matrix}Cl\\OH\end{matrix}$ (see above), is only known in its salts. The potassium salt is formed by heating potassium bichromate (3 parts) for a short period, with concentrated hydrochloric acid (4 parts):—



$$Cr_2O_7K_2 + 2HCl = 2CrO_2\Big\langle\begin{matrix}Cl\\OK\end{matrix} + H_2O.$$

It crystallizes from the solution on cooling in flat, red prisms. Heated to 100° it gives up chlorine. It is decomposed by water into hydrochloric acid and potassium bichromate:—



$$2CrO_2\Big\langle\begin{matrix}Cl\\OK\end{matrix} + H_2O = Cr_2O_7K_2 + 2HCl.$$

Chromium Hexafluoride, $CrFl_6$, corresponds to the trioxide. It may also be regarded as the fluoranhydride of normal chromic acid, $Cr(OH)_6$. It is obtained by heating a mixture of lead chromate and calcium fluoride with fuming sulphuric acid. The resulting dark-red vapor may be condensed in a platinum or lead tube to a very volatile red liquid. It fumes strongly in the air, and with water decomposes into chromic acid and hydrofluoric acid:—

$$CrFl_6 + 3H_2O = CrO_3 + 6HFl.$$

It reacts very energetically with glass.

The chromium compounds can be readily recognized by their color. The following reaction is very characteristic for chromic acid: On adding hydrogen peroxide to a solution of chromium trioxide, or the acidified solution of a chromate, the red liquid is colored blue. The nature of the compound causing this coloration is not known; it is usually assumed to be a higher oxide of chromium. On shaking the blue solution with ether, the latter withdraws the blue compound and is beautifully colored in consequence. The ethereal solution is somewhat more stable than the aqueous. Both are gradually decolorized, with liberation of oxygen.

2. MOLYBDENUM.

$Mo = 95.9$.

Molybdenum occurs rather rarely in nature; usually as molybdenite (MoS_2) and wulfenite (MoO_4Pb). Free molybdenum is obtained as a silver-white metal, of specific gravity 8.6, by igniting the chlorides or oxides in a stream of hydrogen. It is very hard, and fuses at a higher temperature than platinum. When heated in the air it oxidizes to molybdenum trioxide. It is soluble in concentrated sulphuric and nitric acids. It is also converted by the latter into insoluble MoO_3

Like chromium, molybdenum affords compounds of the forms MoX_2, MoX_4 and MoX_6; besides which derivatives are known in which it appears to act as a *pentad* and also as a *triad.*

Molybdenum Dichloride—$MoCl_2$—resulting from the trichloride, $MoCl_3$, when heated in a stream of carbon dioxide (together with $MoCl_4$), is a bright yellow, non-volatile powder. It is converted by potassium hydroxide into the hydrate, $Mo(OH)_2$, a black powder.

Molybdenum Trichloride—$MoCl_3$ or Mo_2Cl_6—produced by gentle heating (at 250°) of $MoCl_5$ in a current of H or CO_2, is a reddish-brown powder, which, when strongly ignited, yields a dark-blue vapor. It dissolves with a beautiful blue color in concentrated sulphuric acid, upon heating, with an emerald green color. Potassium hydroxide converts it into the hydroxide, $Mo(OH)_3$ or $Mo_2(OH)_6$, which forms salts with acids. The ignition of the hydrate affords the black oxide, Mo_2O_3. Strong heating of the trichloride in a current of CO_2 leaves $MoCl_2$ and it sublimes.

Molybdenum Tetrachloride—$MoCl_4$— is a brown, crystalline powder, which appears to break up by evaporation into $MoCl_5$ and $MoCl_3$. It yields a hydrate with ammonium hydroxide, forming salts with acids. The brown solution of the salts readily assumes a blue color by oxidation in the air. The ignition of the hydrate leaves the dioxide, MoO_2, which is converted by nitric acid into the trioxide, MoO_3. *Molybdenum disulphide*, MoS_2, is produced by the ignition of the *trisulphide*, MoS_3, away from air. It is a shining black powder, which occurs native as *molybdenite*, in hexagonal, graphite-like crystals, with a specific gravity of 4.5.

Molybdenum Pentachloride—$MoCl_5$—is prepared by heating MoS_2 or molybdenum in dry chlorine gas. It is a metallic, shining, black, crystalline mass, fusing at 194° and distilling at 268°; its vapor density equals 136, corresponding to the molecular formula $MoCl_5 = 272.6$. It fumes and deliquesces in the air, and dissolves in water with hissing. Its aqueous solution has a brown color. It dissolves in absolute alcohol and ether with a dark-green color.

The *hexachloride*, $MoCl_6$, is not known, but the *oxychlorides*, $MoOCl_4$, and MoO_2Cl_2, are. The first results from the ignition of MoO_2 and carbon in a stream of chlorine, and is a green crystalline mass subliming under 100° and yielding a dark-red vapor.

Bromine forms perfectly analogous compounds with molybdenum.

Molybdenum Trioxide—MoO_3—results on roasting metallic molybdenum or the sulphide in the air. It is a white, amorphous mass, which turns yellow on heating; it fuses at a red heat and then sublimes. It is insoluble in water and acids; but dissolves readily in the alkalies and ammonium hydroxide. When fused with the alkaline hydroxides or carbonates, salts are produced, partly derived from the normal acid, H_2MoO_4, and partly from the polyacids, and correspond to the polychromates:—

$$K_2MoO_4,\ K_2Mo_2O_7,\ K_2Mo_3O_{10},\ Na_2Mo_4O_{13},\ K_6Mo_7O_{24},\ \text{etc.}$$

The *ammonium salt*—$(NH_4)_2MoO_4$—is obtained by dissolving the trioxide in concentrated ammonium hydroxide. In the laboratory it serves as a reagent for phosphoric acid. Alcohol causes it to separate out of its solution in crystals; upon evaporation, however, the salt $(NH_4)_6Mo_7O_{24} + 4H_2O$ crystallizes out. Both salts are decomposed by heat, leaving molybdenum trioxide.

Hydrochloric acid added to a concentrated solution of a molybdate precipitates *molybdic acid*—H_2MoO_4. It is a white, crystalline compound, readily dissolved by an excess of acid. Zinc (tin, stannous chloride, sulphur dioxide) added to this solution causes it to become blue and then green (formation of sesquioxide), in consequence of the formation of lower oxides (like $Mo_3O_8 = 2MoO_3.MoO_2$), and finally brownish-red and yellow, when a suboxide, $Mo_5O_7 = 2MoO_3.MoO$, is produced. The final product, by the action of tin and hydrochloric acid, is molybdenum sesquioxide, Mo_2O_3. Potassium permanganate converts all these lower oxides into molybdic acid.

Molybdic acid can also form polyacids with phosphoric and arsenic acids, *e.g.*, $H_3PO_4.11MoO_3$. These complex phosphomolybdic acids are distinguished by the fact that they form salts insoluble in dilute acids with the metals of the potassium group, with ammonia and with organic bases. On adding a solution containing phosphoric (or arsenic) acid to the nitric acid solution of ammonium molybdate, there is produced a yellow crystalline precipitate of ammonium phospho-molybdate—$(NH_4)_3PO_4.11MoO_3 + 6H_2O$. This reaction serves for the detection and separation of phosphoric acid.

Molybdenum Trisulphide—MoS_3—is thrown down as a brown precipitate from acidulated molybdenum solutions by hydrogen sulphide. It dissolves in alkaline sulphides forming sulpho-salts. Ignited away from air it is converted into molybdenum disulphide, MoS_2, which occurs native as molybdenite.

In addition to these molybdenum compounds in which the element is hexavalent there is a

Molybdenum Tetrasulphide—MoS_4. From this are derived persulphomolybdic acid, MoS_5H_2 and its salts, *e. g.*, MoS_5K_2 and MoS_5KH.

3. TUNGSTEN.

$W = 184$.

Tungsten is found in nature in the tungstates: as wolframite, $FeWO_4$, as scheelite, $CaWO_4$, and as stolzite, $PbWO_4$.

The metal is obtained, like molybdenum, by the ignition of the oxides or chlorides in a stream of hydrogen, in the form of a black powder, or in steel-gray crystalline leaflets, having a sp. gr. 19.1. It is very hard and difficultly fusible. It becomes trioxide when ignited in the air.

Tungsten forms the following chlorides: WCl_2, WCl_4, WCl_5 and WCl_6.

The **Dichloride**—WCl_2—arises by strong ignition of WCl_6 and WCl_4 in a current of carbon dioxide, and is a bright gray, non-volatile mass.

The **Tetrachloride**—WCl_4—obtained by gentle ignition of WCl_6 and WCl_5, in a current of hydrogen or carbon dioxide, is grayish-brown and upon sublimation decomposes into WCl_2 and volatile WCl_5. It forms a brown oxide (WO_2) with water.

The **Pentachloride**—WCl_5—is obtained by the distillation of WCl_6 in a current of hydrogen or carbon dioxide, and consists of shining, black, needle-like crystals. It fuses at 248° and boils at 275°, forming a dark-brown vapor, with the density 180 ($WCl_5 = 360.4$). It affords an olive-green solution and a blue oxide, W_2O_5, with water. It dissolves with a deep blue color in carbon disulphide.

Tungsten Hexachloride—WCl_6—is produced when the metal or a mixture of wolframite with carbon is heated in a current of chlorine. It forms a dark violet, crystalline mass, fusing at 275° and boiling at 346°. The vapor density equals 198 ($WCl_6 = 395.8$). It dissolves in carbon disulphide with a reddish-brown color; it forms WO_3 with water.

The Oxychloride—WCl_4O—consists of red crystals, fusing at 210° and boiling at 227°; its vapor density equals 170 ($WCl_4O = 341$). **The Dioxychloride**—WCl_2O_2—sublimes in bright yellow, shining leaflets.

Tungsten Trioxide—WO_3—is thrown out of the hot solution of tungstates by nitric acid, as a yellow precipitate insoluble in acids, but dissolving readily in potassium and sodium hydroxides. **Tungstic acid**, $WO(OH)_4$, is, however, precipitated from the cold solution, but on standing over sulphuric acid it becomes $WO_2(OH)_2$ and at 100° passes into ditungstic acid, $W_2O_7H_2 = W_2O_5(OH)_2$.

When tungstic acid is reduced in hydrochloric acid solution by zinc it first becomes blue (formation of W_2O_5) and then brown, when the salt of the dioxide, WO_2, is formed. Potassium permanganate oxidizes this to tungstic acid.

The salts of tungstic acid are perfectly analogous to the molybdates and are derived from the normal acid or the polyacids. The *normal sodium salt*, $Na_2WO_4 + 2H_2O$, and the so-called *meta-tungstate of sodium*, $Na_2W_4O_{13} + 10H_2O$, are applied practically. Materials saturated with their solutions do not burst into a flame, but smoulder away slowly.

The reduction of the tungstates (by fusion with tin, etc.) affords peculiar compounds, *e. g.*, $K_2W_3O_9$ or $K_2W_4O_{12}$; these have various colors, possess metallic lustre, and are applied as tungsten bronzes.

Tungstic acid also combines with phosphoric and arsenic acids, forming derivatives analogous to those of molybdic acid with the same acids.

The metal is used in the manufacture of tungsten steel: a slight quantity of it increases the hardness of the latter very considerably.

4. URANIUM.

Ur or U = 239.4.

In nature it occurs chiefly as uraninite, a compound of uranic and uranous oxides—$UO_2.2UO_3 = U_3O_8$. This mineral has been discovered to contain as high as 3% of nitrogen.

The metal is obtained by heating uranous chloride with sodium. It has a steel-gray color and a specific gravity of 18.7. When heated in the air it burns to uranous-uranic oxide. Its specific heat equals 0.0267, and its atomic volume is therefore 6.6. It melts about 1500°. There are two series of uranium compounds. In the one, the metal is a tetrad UX_4; these uranous or urano-compounds are very unstable, and pass readily into the uranic or derivatives of hexavalent uranium. Uranous oxide is of a basic nature, and only forms salts with acids.

The compounds of hexavalent uranium are called the uranic compounds. UO_3 and $UO_2(OH)_2$ have a predominant basic character, but are also capable of forming salts with bases which are called *uranates*. In the salts derived from acids, *e. g.*, $UO_2(NO_3)_2$ and UO_2SO_4, the group UO_2 plays the rôle of a metal; it is called *uranyl*, and its salts are termed *uranyl salts*. They may also be regarded as basic salts.

URANOUS COMPOUNDS.

Uranous Chloride—UCl_4—is obtained by heating metallic uranium in a stream of chlorine, or uranous oxide in hydrochloric acid. It consists of dark green octahedra with metallic lustre. It volatilizes at a red heat, forming a red vapor, whose density agrees with the formula UCl_4. It deliquesces in the air, and dissolves with hissing in water. Uranous hydroxide remains when the solution is evaporated.

Uranous Oxide—UO_2—is formed when the other oxides are heated in a current of hydrogen. It is a black powder, which becomes uranous-uranic oxide, $UO_2.2UO_3$, when heated in the air.

Uranous oxide dissolves with a green color in hydrochloric and concentrated sulphuric acids. *Uranous sulphate*, $U(SO_4)_2 + 8H_2O$, consists of green crystals. From the salts the alkalies precipitate the voluminous, bright green *uranous hydroxide*, $U(OH)_4$, which becomes brown on exposure.

HEXAVALENT URANIUM COMPOUNDS.

Uranium Hexachloride—UCl_6—has not been obtained, but the **oxychloride**, UO_2Cl_2 (Uranyl chloride), exists ; it is obtained by heating UO_2 in dry chlorine gas, or by the evaporation of uranyl nitrate with hydrochloric acid. It is a yellow crystalline mass, deliquescing in the air.

Uranic Oxide, UO_3 or **Uranyl oxide**, UO_2 O—is a yellow powder, and is obtained by heating uranyl nitrate to 250°. When warmed with nitric acid it becomes *uranyl hydrate* or *uranic acid*, $UO_2(OH)_2$, which is also yellow-colored.

Uranyl Nitrate—$UO_2(NO_3)_2$—results from the solution of uranous or uranic oxide, or more simply of uraninite in nitric acid. It crystallizes with six molecules of water, in large, greenish-yellow prisms, which are readily soluble in water and alcohol. On adding sulphuric acid to the solution, **Uranyl sulphate**—$UO_2SO_4 + 6H_2O$—crystallizes out, on evaporation, in lemon-yellow needles.

If sodium or potassium hydroxide be added to the solutions of uranyl salts, yellow precipitates of the *uranates* —$U_2O_7K_2$ and $U_2O_7Na_2$—are obtained. These are soluble in acids. In commerce the sodium salt is known as uranium yellow, and is employed for the yellow coloration of glass (uranium glass) and porcelain. The uranates can be obtained in crystalline form, by igniting uranyl chloride with alkali chlorides in the presence of ammonium chloride. Zinc and sulphuric acid reduce uranic to uranous compounds.

The so-called *uranic-uranous oxide*, which constitutes uraninite, and is formed by the ignition of the other oxides in the air, must be viewed as uranous uranate—$2UO_3.UO_2 = (\overset{\text{VI}}{U}O_2.O_2)_2 \overset{\text{IV}}{U}$.

Many uranium salts exhibit magnificent fluorescence. The oxide colors glass fluxes a beautiful greenish-yellow (uranium glass). Uranous oxide—UO_2—imparts a beautiful black color to glass and porcelain.

Besides these compounds, in which uranium appears to be tetravalent and hexavalent, it also affords a *pentachloride*, UCl_5, like molybdenum and tungsten. The same results on conducting chlorine gas over a moderately heated mixture of carbon with one of the uranium oxides. It consists of dark needles which, in direct light, are metallic green, but in transmitted, ruby red. It deliquesces in the air to a yellowish-green liquid ; upon heating it is dissociated into UCl_4 and Cl (at 120°–235°).

There is also a *tetroxide*, UO_4, which, like the trioxide, UO_3, yields salts with the bases. It corresponds to molybdenum tetrasulphide MoS_4 (p. 386).

MANGANESE.

$Mn = 54.8$ (55.0).

According to its atomic quantity, manganese bears the same relation to the elements of the chlorine group as chromium to the elements of the sulphur group. The relationship manifests itself distinctly in the higher states of oxidation. Permanganic oxide, Mn_2O_7, and acid, $HMnO_4$, are perfectly analogous to Cl_2O_7 (or I_2O_7) and $HClO_4$. The permanganates and the perchlorates are very similar, and for the most part are isomorphous. The manganese in them appears to be heptavalent, like the halogens in their highest state of oxidation. The similarity of manganese to the halogens is restricted to this one point of resemblance. In the rest of its derivatives, manganese shows great resemblance to the elements standing in the same horizontal series of the periodic system, viz., with iron and chromium (p. 349). Like these two elements, it forms three series of compounds.

1. In the manganous derivatives—MnX_2—the metal is divalent. These salts are the more stable, and comprise the most common manganese compounds. They resemble and are usually isomorphous with the *ous* salts of iron and chromium, and the salts of metals of the magnesium group (p. 314).
2. The manganic compounds—Mn_2X_6—are similar to and isomorphous with the ferric, chromic and aluminium derivatives; they are, however, less stable, and easily reduced to the manganous state. Their composition is due to the tetravalent nature of manganese (p. 377).
3. The derivatives of manganic acid—$H_2MnO_4 = MnO_2(OH)_2$, in which manganese is hexavalent—are analogous to those of ferric (H_2FeO_4) and chromic acid (H_2CrO_4), and, of course, to those of sulphuric acid (H_2SO_4).

Consequently, in manganese we plainly observe how the similarity of the elements in their compounds is influenced by the valence (see p. 333). In its *ous* condition, manganese, like the elements of the magnesium group, has a rather strong basic character, which diminishes considerably in the *ic* state. Hexavalent manganese has a metalloidal acidic character, and, in manganic acid, approaches sulphur. By the further addition of oxygen, manganese finally (in permanganic acid) acquires the metalloidal character of the halogens. We have already noticed that many other metals, especially chromium and iron, exhibit a similar behavior. Osmium tetroxide, OsO_4, wholly resembles the halogens.

On the other hand, the metalloidal and the weak basic metals acquire a strong basic, alkaline character, by the addition of hydrogen, or hydrocarbon groups (CH_3, C_2H_5). The groups, NH_4 (ammonium), $P(CH_3)_4$ (tetramethylphosphonium), $S(C_2H_5)_3$ (triethylsulphine), $Sn(C_2H_5)_3$ (tin triethyl), etc., are of metallic nature, because their hydroxides, $P(CH_3)_4.OH$, $S(C_2H_5)_3.OH$, $Sn(C_2H_5)_3.OH$, are perfectly similar to the hydroxides (KOH, $NaOH$) of the alkali metals.

Manganese is widely distributed in nature. It is found native in meteorites. Its most important ores are pyrolusite, MnO_2, hausmannite, Mn_3O_4, braunite, Mn_2O_3, manganite, $Mn_2O_3.H_2O$, and rhodochroisite, $MnCO_3$.

Metallic manganese is obtained by igniting the oxides with charcoal. It has a grayish-white color, is very hard, and fuses with difficulty; specific gravity 7.2. It oxidizes readily in moist air. It decomposes water on boiling, and, when dissolved in acids, forms manganous salts.

The heat of formation of the most important manganese compounds corresponds to the symbols :—

$(Mn,O,H_2O) = 94.7$ $(Mn,Cl_2) = 111.9$ $(Mn,Cl_2,Aq.) = 128.0$.
$(Mn,O_2,H_2O) = 116.2$ $(Mn,S,O_4) = 249.8$ $(Mn,O_4,K) = 194.8$.

MANGANOUS COMPOUNDS.

Manganous Oxide—MnO—results from ignition of the carbonate, with exclusion of air, and by heating all manganese oxides in hydrogen. It is a greenish, amorphous powder, which, in the air, readily oxidizes to Mn_3O_4.

Manganous Hydroxide—$Mn(OH)_2$—is a voluminous, reddish-white precipitate, formed by the alkalies in manganous solutions. When exposed to the air, it oxidizes quickly to manganic hydroxide, $Mn_2(OH)_6$.

Manganous salts usually have a pale, reddish color, and are formed by the solution of manganese or manganic oxides in acids.

Manganous Chloride—$MnCl_2$—crystallizes with four molecules of water in reddish tables. On drying, it is decomposed with separation of hydrochloric acid. Anhydrous manganous chloride is prepared by igniting the double salt $MnCl_2.2NH_4Cl + H_2O$ (see Magnesium Chloride), or by heating manganese oxides in hydrochloric acid gas; it is a crystalline, reddish mass, which deliquesces in the air.

Manganous Sulphate—$MnSO_4$—crystallizes below + 6° with 7 molecules of H_2O (like magnesium and ferrous sulphates), and at ordinary temperatures with $5H_2O$ (like copper sulphate); the last molecule of water does not escape until 200°. It forms double salts with the alkaline sulphates, *e. g.*, $MnSO_4.K_2SO_4 + 6H_2O$.

Manganous Carbonate—$MnCO_3$—exists in nature as rhodochroisite, and is precipitated by alkaline carbonates from manganous solutions, as a white powder, which turns brown on exposure.

Manganous Sulphide—MnS—is found in nature as alabandite or manganese blende. Alkaline sulphides precipitate a flesh-colored sulphide from manganese solutions. It becomes brown in the air.

MANGANIC COMPOUNDS.

Manganic Oxide—Mn_2O_3, manganese sesquioxide—is a black powder produced by the ignition of the manganese oxides in a current of oxygen gas. It occurs as *Braunite* in dark-brown quadratic crystals.

Manganic Hydroxide—$Mn_2(OH_6)$ or $Mn(OH)_3$, manganic hydrate—is precipitated by ammonium hydroxide from manganous solutions containing ammonium chloride as a dark-brown mass. It dissolves in cold hydrochloric acid to a dark-brown liquid, containing, in all probability, *manganic chloride*, $MnCl_3$ or Mn_2Cl_6. When this is heated it decomposes into $MnCl_2$ and chlorine.

Manganite, occurring in iron-black crystals, is the hydroxide, $Mn_2O_2(OH)_2$ or $MnO.OH$.

Manganous-manganic Oxide—$Mn_3O_4 = MnO.Mn_2O_3$. It constitutes the mineral *hausmannite*, crystallized in dark-gray quadratic octahedra, and is obtained as a reddish-brown powder by the ignition of all other manganese oxides in the air. It reacts with hydrochloric acid, according to the equation :—

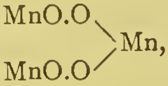
$$Mn_3O_4 + 8HCl = 3MnCl_2 + 4H_2O + Cl_2.$$

Since manganic oxide is quadratic in its crystallization, while all other sesquioxides (like corundum and hematite) are rhombohedral, and since the first is decomposed by dilute nitric and sulphuric acids into MnO_2 and a manganous salt, it has been generally supposed that manganic oxide is not a sesquioxide, but rather a compound of the dioxide with manganous oxide :—

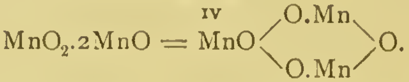
$MnO_2.MnO =$

Hausmannite is quadratic, while other metallic oxides (the spinels, p. 354 and p. 379, and magnetite, Fe_3O_4) are isometric ; therefore the former is not considered a compound of manganese sesquioxide and protoxide :—

$Mn_2O_3.MnO =$



but as manganous oxide and the dioxide :—



This is shown by its behavior toward dilute nitric and sulphuric acids, which decompose it into manganese dioxide, and two molecules of manganous oxide. Chrysoberyl, unlike other spinels, is trimetric, and other reactions clearly prove (chiefly their deportment with concentrated sulphuric acid) that manganic and mangano manganic oxides are to be regarded as sesquioxide derivatives.

Manganic oxide, like the other sesquioxides, is a very feeble base, which does not afford salts with dilute or weak acids, and by separation of oxygen reverts to the manganous condition. Its salts are very unstable.

Manganic Sulphate—$Mn_2(SO_4)_3$—is obtained by the solution of manganic oxide, hydroxide, or, better, manganous-manganic oxide in concentrated sulphuric acid. When the last oxide is employed manganous sulphate also results. The best procedure is to heat the hydrate of manganese dioxide (see below) with concentrated sulphuric acid to 168°, when the sulphate will separate as an amorphous, dark-green powder. It dissolves with a dark-red color in a little water. It forms *alums*, with potassium and ammonium sulphates—*e. g.*, $Mn_2(SO_4)_3.K_2SO_4 + 24H_2O$. Much water will decompose these with the separation of manganic hydroxide.

Manganese Dioxide—MnO_2—peroxide. This is the mineral pyrolusite, occurring in dark-gray radiating masses, or in almost black rhombic prisms, which possess metallic lustre. When gently heated it is converted into oxide, by strong ignition into manganous-manganic oxide :—

$$3MnO_2 = Mn_3O_4 + 2O.$$

It is used for making oxygen. Manganous oxide results at a white heat. Chlorine escapes when it is warmed with hydrochloric acid :—

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

The dioxide may be obtained artificially by heating manganous nitrate to 150–160°. Its hydrates—$MnO_2.H_2O$ and $MnO_2.2H_2O$—are produced on adding a hypochlorite to the solution of a manganous salt, or if chlorine be conducted through a solution of manganese containing sodium carbonate, or by adding $KMnO_4$ to a boiling solution of a manganous salt. The precipitated dioxide dissolves in cold hydrochloric acid, without liberating chlorine, as

$MnCl_4$ is probably formed; when heat is applied it breaks up into $MnCl_2$ and Cl_2. This deportment would indicate that manganese is tetravalent in the dioxide. Manganese dioxide also unites with bases, affording the so-called *manganites*, *e. g.*, Mn_2O_5Ba and $Mn_2O_5K_2$.

Manganese peroxide (also Mn_2O_3 and Mn_3O_4) serves chiefly for the manufacture of chlorine gas, and it is, therefore, important from a technical point to estimate the quantity of chlorine which a given dioxide of manganese is able to set free. This is done by boiling the oxide with hydrochloric acid, conducting the liberated chlorine into a potassium iodide solution, and determining the separated equivalent amount of iodine by means of sodium hyposulphite. Or the oxide is heated in a flask with oxalic and sulphuric acids, when the oxalic acid is oxidized to carbon dioxide, and from the quantity of this set free we can calculate the quantity of active or available oxygen in the manganese oxide.

In the preparation of chlorine the manganese is found in the residue as manganous chloride. With the relatively high value of pyrolusite, it is important for trade that the peroxide be recovered from the residue. This regeneration is at present largely executed by the method proposed by Weldon, according to which the manganous chloride, containing excess of hydrochloric acid, is neutralized with lime, the clear liquid brought into a high iron cylinder (the oxidizer), milk of lime added and air forced in. The mixture becomes warm, and so-called calcium manganite, $MnO_3Ca = MnO_2.CaO$, is precipitated as a black mud:—

$$MnCl_2 + 2CaO + O = MnO_3Ca + CaCl_2.$$

The calcium chloride solution is run off, and the residual calcium manganite employed for the preparation of chlorine, when it conducts itself as a mixture of $MnO_2 + CaO$.

COMPOUNDS OF MANGANIC AND PERMANGANIC ACID.

When oxygen compounds of manganese are heated in the air in contact with potassium hydroxide, or, better, with oxidizing substances, like nitre or potassium chlorate, a dark-green amorphous mass is produced, which dissolves in cold water, with a dark-green color. When this solution is evaporated under the air-pump, dark-green metallic rhombic prisms of **potassium manganate**—K_2MnO_4—crystallize out. This salt is isomorphous with potassium sulphate and chromate. It suffers no change by solution in potassium or sodium hydroxide, but is decomposed by water, brown hydrated manganese dioxide separating, and the green solution of the manganate changing into a dark-red solution of the permanganate, $KMnO_4$:—

$$3K_2MnO_4 + 3H_2O = 2KMnO_4 + MnO_2.H_2O + 4KOH.$$

A similar conversion of the green manganate into red permanganate occurs more rapidly under the influence of acids:—

$$3K_2MnO_4 + 4HNO_3 = 2KMnO_4 + MnO_2 + 4KNO_3 + 2H_2O.$$

Owing to this ready alteration in color the solution of the manganate is called *chameleon mineral.*

Potassium Permanganate—$KMnO_4$—is best prepared by conducting CO_2 into the manganate solution until the green color has passed into a red. When the solution is concentrated the salt crystallizes in dark-red rhombic prisms isomorphous with potassium perchlorate, $KClO_4$. It is soluble in twelve parts of water at ordinary temperatures.

The permanganate solution is a strong oxidizing agent, converting lower oxygen compounds into higher, and in doing this it is reduced to a colorless manganous salt. When a permanganate solution is added to an acidulated ferrous solution, the former is decolorized, and there results a faintly yellow-colored solution of ferric and manganous salts:—

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O + K_2SO_4.$$

Hence the solution of this salt serves for the volumetric estimation of ferrous salts.

In the same manner, the permanganate oxidizes and destroys many organic substances, therefore its solution cannot be filtered through paper; it serves as a disinfectant.

The permanganate is also reduced by hydrogen peroxide (p. 105); the reaction proceeds according to the following equation:—

$$Mn_2O_7K_2O + 5H_2O_2 = 2MnO + K_2O + 5H_2O + 5O_2;$$

the formation of oxides requires the presence of acids (sulphuric acid) for the completion of the reaction.

The remaining permanganates are similar to and isomorphous with the perchlorates. The sodium salt is very soluble in water, and does not crystallize well.

Very cold sulphuric acid added to dry permanganate causes the separation of **Manganese Heptoxide**—Mn_2O_7—an oily, dark-colored liquid. By careful warming it is converted into dark-violet vapors, which explode when heated rapidly. Manganese heptoxide has a violent oxidizing action; paper, alcohol and other organic matter are inflamed by mere contact with it.

METALS OF GROUP VIII.

Of the known elements, those standing in the eighth column of the periodic system remain for consideration (p. 249):—

Fe = 56	Co = 58.6	Ni = 58.6
Ru = 101.7	Rh = 103.0	Pd = 106
Os = 192	Ir = 193.2	Pt = 194.8

These elements are the middle members of the three great periods, and they have no analogues in the two short periods (pages 246, 248).

As regards both atomic weights and physical and chemical deportment, these elements constitute a transition from the preceding members of the great periods (Mn and Cr, Mo, W) to the next following members (Cu, Ag, Au, and Zn, Cd, Hg, p. 324). The elements standing side by side (heterologous) and belonging to the same periods are very similar in their physical properties, and show, *e. g.*, very close specific gravities. They are, therefore, usually arranged in groups, and distinguished as, (1) the iron group (Fe, Co, Ni), with the specific gravity 7.8–8.6; (2) the group of the light platinum metals (Ru, Rh, Pd), with the specific gravity 11.8–12.1, and (3) the group of the heavy platinum metals (Os, Ir, Pt), with the specific gravity 21.1–22.4.

On the other hand, the homologous elements (Fe, Ru, Os; Co, Rh, Ir; and Ni, Pd, Pt) show a like similarity in their chemical properties, as do the other homologous groups, and therefore may be considered in such groups. This resemblance shows itself chiefly in their combination forms, and, of course, too, in the properties of the compounds (p. 333). We know that the metals of group VI (chromium, molybdenum, tungsten) and of group VII (manganese) form the highest oxides (MeO_3 and Me_2O_7) having an acidic nature. In the adjacent elements of group VIII (iron, ruthenium, and osmium) we find salts:—

$$FeO_4K_2,\ RuO_4K_2,\ OsO_4K_2,$$

derived from the unstable trioxides FeO_3, RuO_3 and OsO_3. This acid-forming function disappears in the following members, Co, Rh, Ir, and Ni, Pd, Pt; their chemical valence diminishes rapidly and they attach themselves to Cu, Ag and Au.

Consequently the whole physical and chemical deportment of the 9 elements about to be considered is governed by their position in the periodic system.

As mentioned on pp. 247, 252 and at other places, the valences of the elements in their highest salt-forming oxides present themselves as periodic functions of the atomic weights. A similar dependence is also seen in the lowest salt-forming oxides, and may be observed in the following tabulation of both classes of oxides of the middle members of the great periods:—

$\overset{\text{V}}{V_2O_5}$	$\overset{\text{VI}}{CrO_3}$	$\overset{\text{VII}}{Mn_2O_7}$	$\overset{\text{VI}}{FeO_3}$	$\overset{\text{IV}}{Co_2O_3}$	$\overset{\text{II}}{NiO}$	$\overset{\text{II}}{CuO}$	$\overset{\text{II}}{ZnO}$	$\overset{\text{III}}{Ga_2O_3}$	$\overset{\text{IV}}{GeO_2}$
$\overset{\text{III}}{V_2O_3}$	$\overset{\text{II}}{CrO}$	$\overset{\text{II}}{MnO}$	$\overset{\text{II}}{FeO}$	$\overset{\text{II}}{CoO}$		$\overset{\text{I}}{Cu_2O}$			$\overset{\text{II}}{GeO}$

$\overset{V}{Nb_2O_5}$	$\overset{VI}{MoO_3}$	—	$\overset{VI}{RuO_3}$	$\overset{IV}{Rh_2O_3}$	$\overset{II}{PdO}$	$\overset{I}{Ag_2O}$	$\overset{II}{CdO}$	$\overset{III}{In_2O_3}$	$\overset{IV}{SnO_2}$
$\overset{III}{(Nb_2O_3)}$	$\overset{II}{MoO}$	—	$\overset{II}{RuO}$	$\overset{II}{RhO}$					$\overset{II}{SnO}$
Ta_2O_5	$\overset{VI}{WO_3}$	—	$\overset{VI}{OsO_3}$	$\overset{IV}{IrO_2}$	$\overset{IV}{PtO_2}$	$\overset{III}{Au_2O_3}$	$\overset{II}{HgO}$	$\overset{III}{Tl_2O_3}$	$\overset{IV}{PbO_2}$
$\overset{III}{(Ta_2O_3)}$	$\overset{II}{(WO)}$	—	$\overset{II}{OsO}$	$\overset{II}{IrO}$	$\overset{II}{PtO}$	$\overset{I}{Au_2O}$	$\overset{I}{Hg_2O}$	$\overset{I}{Tl_2O}$	$\overset{II}{PbO}$.

METALS OF THE IRON GROUP.

The metals of this group, iron, cobalt and nickel, form a gradual transition from manganese to copper. Their magnetic properties distinguish them from the other elements.

Iron forms three series of compounds after the forms, FeO_3, Fe_2O_3 and FeO. In its highest combinations iron has an *acidic* character, and the derivatives of ferric acid (H_2FeO_4) are perfectly similar to those of chromic and manganic acids (p. 389); they are, however, less stable than the latter. Their analogues with cobalt and nickel are unknown.

The ferr*ic* compounds—Fe_2X_6—containing the hexavalent group $\overset{VI}{Fe_2}$ (p. 377), are much like the aluminium, chromic and manganic derivatives. They are generally isomorphous with them. They are characterized among iron salts by their relative stability. The highest oxides of cobalt are far less stable, and only a few double salts of this form are known, while the higher salts with nickel are unknown.

Again, iron, cobalt, and nickel afford *ous* compounds, (FeX_2, CoX_2, NiX_2) in which they appear to be dyads. They resemble the compounds of chromium, manganese, and copper of the same form, and those of the magnesium metals. The ferrous salts are not as stable as the ferric; they are readily oxidized to the latter.

The cobaltous and nickelous compounds are quite stable, and in this respect these metals ally themselves with copper and zinc.

1. IRON.

Fe = 56.

This metal, of such great practical importance, is very widely distributed in nature. It is found native on the earth's surface almost exclusively in meteorites; it is, however, present in great masses in other worlds which (like the sun) are surrounded by an atmosphere of hydrogen.

The most important iron ores are: magnetite (Fe_3O_4), hematite (Fe_2O_3), brown iron ore and limonite (hydrates of the oxide) and siderite ($FeCO_3$). These ores constitute almost the sole material for the manufacture of iron; the sulphur ores, like pyrite, are less adapted to this end.

In commerce there are three varieties of iron: cast-iron, steel, and wrought-iron. Their chief chemical difference is in the variable quantity of carbon contained in them.

Cast-iron contains 3–6 per cent. carbon, in part chemically combined, and in part mechanically mixed in the form of graphite. When molten cast-iron is cooled rapidly it yields the so-called *white iron*, in which the greater portion of the carbon is chemically combined with the iron. It has a whitish color, exhibits a granular crystalline structure upon fracture, and is very hard and brittle. Its specific gravity is 7.1. It fuses to a pasty mass about 1200°, and is on this account not suited for castings. The chemically combined carbon in it can easily be removed by oxidation, and, therefore, it is adapted for the manufacture of steel or wrought iron.

When molten cast-iron is allowed to cool slowly, the greater part of the carbon in it separates in the form of small leaflets of graphite. The *gray* cast-iron produced in this way has a darker gray color, is not so hard and brittle, fuses more readily (about 1150°) than white cast-iron, and serves for the manufacture of castings. Neither variety can be forged or welded, on account of its brittleness.

Steel contains 0.8–1.8 per cent. of carbon, all of which is chemically combined with the iron. It has a steel-gray color and a fine-grained structure; its specific gravity equals 7.6–8.0. It fuses with more difficulty (about 1400°) than cast-iron, but easier than wrought-iron. When molten steel is rapidly cooled, it becomes very hard and brittle. In this process more carbon is chemically combined. If cooled slowly, it is soft and malleable, and may be forged and welded. Welding becomes more and more difficult with the addition of carbon.

Wrought-iron contains the least amount of carbon, 0.2–0.6 per cent. It possesses a bright-gray color, has a specific gravity of 7.6, is rather soft and tough, and, at a red heat, may be readily forged, rolled, and welded. The rolled iron possesses a fibrous texture, while the forged is fine grained; the former is more compact and tenacious. Wrought-iron fuses at a bright white heat (1500°).

Metallurgy of Iron.—The extraction of iron from its oxygen ores is based upon the reduction of the same by carbon at a red heat. In the oldest method, the ores were heated with carbon in wind furnaces; in this way the excess of heat consumed the greater portion of the carbon, and the product was an iron poor in carbon, wrought-iron, a spongy mass, which was then forged under the hammer. The present methods were adopted since the beginning of the previous century. According to these cast-iron is first prepared from the ores, and this afterwards converted into steel or wrought-iron. The smelting of the ores is executed in large, walled blast furnaces, that permit the process to proceed without interruption. The furnaces are filled from openings above, with alternating layers of coal, broken ore and fluxes containing silica and lime; the latter facilitate the melting together of the reduced iron. The air necessary for the process is blown into the contracted portion of the furnace by means of a blast engine. The combustion of the coal affords carbon monoxide, which reduces the iron oxides to metal:—

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2.$$

As the reduced iron sinks in the furnace it comes in contact with the coal, takes up carbon and forms cast-iron, which fuses as it sinks lower and flows into the hearth of the furnace. Protracted and strong heating converts the chemically united carbon into the graphitic form, and thus accelerates the formation of the gray cast-iron. The earthy impurities of the ores combine with the fluxes to a readily fusible *slag*, which envelops the fused iron and protects it from oxidation.

To convert the cast-iron thus produced into steel or wrought-iron, carbon must be withdrawn from it. In making the wrought-iron the cast-iron is fused in open hearths (refining process), or in reverberatory furnaces with air access, and the mass stirred thoroughly until it has become semi-pasty (puddling process). In this way almost all the carbon is burned to carbon monoxide and the other admixtures, like silicon, sulphur, and phosphorus, present in small quantities, are oxidized. The wrought-iron is then worked up by rolling, or under the iron hammers (bar-iron).

Steel was formerly manufactured from wrought-iron (not cast-iron), by cementation. The iron bars, mixed with fine charcoal, were exposed to a red heat, when the iron took up carbon from the surface. The bars were then reforged, again heated with fine charcoal, and the process repeated until the mass became as homogeneous as possible (cementation steel). A more uniform steel is obtained if it be fused in crucibles (cast-steel).

At present, steel is chiefly prepared directly from cast-iron, by the method invented by Bessemer, somewhere in 1850. It consists in blowing air, under high pressure, into the molten iron, until the necessary amount of carbon has been consumed (Bessemer steel).

An iron rich in silicon (1.5–2% Si) is well adapted to the purpose, because by the simultaneous combustion of the silicon the temperature is considerably augmented. The operation is conducted in a pear-shaped vessel known as the converter. The air is blown in through openings in the bottom. The decarbonization is only partial in this way. This is better accomplished by the English method, which removes the carbon so as to convert the mass into wrought iron, and then it is again carbonized by adding molten spiegeleisen.

The Bessemer process is only adapted to crude iron containing as little sulphur and phosphorus as possible (at the highest, .05% P), because in this process this phosphorus is not consumed, but remains unaltered in the steel. By a slight, yet very essential alteration, Thomas and Gilchrist (1880) rendered it suitable for iron containing much phosphorus. Their process is now known as the "basic process," and consists in lining the converter with a basic lining material, composed of clay and silica, mixed with lime and magnesia. By contact with these substances (bases) the iron is completely dephosphorized and the phosphorus changed to calcium phosphate.

All the phosphorus contained in iron ores collects in the slag of the converter.

The latter contains as much as 15–20 % phosphoric acid (and may even be increased to 30 %), existing as calcium phosphate, and this may be applied as a fertilizer in agriculture.

A third method of making steel consists in puddling the different varieties of iron together, or with iron ores. Martin steel is obtained by fusing cast-iron with wrought-iron. It is much used. Uchatius steel is prepared by fusing cast-iron together with some iron ore and pyrolusite.

The various and more recent processes for manufacturing steel and wrought-iron, the knowledge that their difference is mainly in hardness, and that the so-called Bessemer steel is not tempered, have led to the introduction of a new division and nomenclature for these substances (which are difficultly fusible and malleable compared with cast-iron). We now distinguish :—

(1) *Weld iron* as a non-fused, non-tempered mass, formerly wrought-iron; (2) *weld steel*, not fused, tempered, formerly puddle steel; (3) *ingot iron*, fused, not tempered, formerly Bessemer steel; (4) *ingot steel*, has been fused and tempered.

Ordinary iron, even the purest wire, always contains foreign ingredients, principally carbon and manganese, and minute quantities of silicon, sulphur, phosphorus, nitrogen, nickel, cobalt, titanium and others. The quantity of manganese is purposely increased (to 30 per cent.), as by this means the iron acquires valuable technical properties; it becomes more compact and solid. When iron, containing carbon, is dissolved in hydrochloric acid the chemically combined carbon unites with hydrogen, forming hydrocarbons, while the mechanically admixed graphite remains behind. The whole quantity of carbon is determined by the solution of the iron in bromine water or cupric chloride, when all the carbon remains behind.

To prepare chemically pure iron, heat the pure oxide or the oxalate in a current of hydrogen :—

$$Fe_2O_3 + 3H_2 = 2Fe + 3H_2O;$$

the iron then remains as a fine black powder. If the reduction occurs at a red heat, the powder glows in the air, and burns (pyrophoric iron). The strongly ignited powder is not inflammable. Iron obtained by the electrolysis of ferrous sulphate contains some hydrogen.

Chemically pure iron has a grayish white color, is tolerably soft, and changes but slowly in the air. Its specific gravity is 7.78. It melts in an oxy-hydrogen flame at 1800°. Ordinary iron rusts rapidly in moist air, as it covers itself with a thin layer of ferric hydroxide. When ignited in the air it is coated with a layer of ferrous-ferric oxide (Fe_3O_4) which is readily detached. It burns with an intense light in oxygen.

In contact with a magnet iron becomes magnetic; steel alone retains the magnetism, while cast-iron and wrought-iron soon lose the property after the removal of the magnet.

Iron decomposes water at a red heat, with the formation of ferrous-ferric oxide, and the liberation of hydrogen :—

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

The metal dissolves without trouble in hydrochloric and sulphuric acids, with evolution of hydrogen ; the latter has a peculiar odor, due to hydrocarbons that are liberated at the same time. Iron dissolves in nitric acid with separation of nitric oxide. On dipping iron into concentrated nitric acid, and then washing it with water, it is no longer soluble in the acid (passive iron) ; this phenomenon is probably due to the production of ferrous oxide upon its surface.

Metallic iron unites with carbon monoxide, forming $Fe(CO)_5$, *ferro-pentacarbonyl.* This is a liquid boiling at 102.8° and solidifying below —21°. It is decomposed on exposure to the light, with the formation of yellow-colored flakes, which probably have the formula $Fe_2(CO)_7$ (*Chem. Jour.* 59, 1090).

FERROUS COMPOUNDS.

These are produced by the solution of iron in acids, and may also be obtained by the reduction of ferric salts :—

$$Fe_2Cl_6 + Zn = 2FeCl_2 + ZnCl_2.$$

In the hydrous state they are usually of a green color ; in the air they oxidize to ferric salts :—

$$2FeO + O = Fe_2O_3.$$

Ferrous Chloride—$FeCl_2$—crystallizes from aqueous solutions in green monoclinic prisms, with four molecules of water. These deliquesce in the air and oxidize. When dried they sustain a partial decomposition. The anhydrous salt is formed by conducting hydrogen chloride over heated iron. It is a white mass, which fuses on application of heat and sublimes at a red heat in white, six-sided leaflets. Its vapor density at 1300–1500° corresponds to the formula $FeCl_2$, but it appears that at lower temperatures it is also possible for the molecules Fe_2Cl_4 to exist.

It forms double salts with the alkaline chlorides, *e. g.* :—

$$FeCl_2.2KCl + 2H_2O.$$

Ferrous Iodide—FeI_2—is obtained by warming iron with iodine and water. It crystallizes with four molecules of water.

Ferrous Oxide—FeO—is a black powder, resulting from the reduction of ferric oxide by carbon monoxide. When warmed it oxidizes readily. **Ferrous Hydroxide**—$Fe(OH)_2$—is thrown out of ferrous solutions by the alkalies, as a greenish-white precipitate. Exposed to the air, it oxidizes, becoming green at first, then reddish-brown. It is somewhat soluble in water, and has an alkaline reaction.

Ferrous Sulphate—$FeSO_4$—crystallizes with 7 molecules of H_2O in large, greenish, monoclinic prisms, and is generally called *green vitriol.* The crystals effloresce somewhat in dry air. They oxidize in moist air, and become coated with a brown layer of basic ferric sulphate. At 100° they lose 6 molecules of H_2O, and change to a white powder. The last molecule of water escapes at 300°. Therefore, ferrous sulphate behaves just like the sulphates of the metals of the magnesium group. Like them, it unites with alkaline sulphates to double sulphates, which contain six molecules of water, *e.g.*, $SO_4Fe.SO_4K_2 + 6H_2O$. These are more stable than ferrous sulphate, and oxidize very slowly in the air.

Ferrous sulphate is obtained by dissolving iron in dilute sulphuric acid; or from pyrites (FeS_2). When the latter are roasted they lose one molecule of sulphur, and are converted into ferrous sulphide (FeS), which, in the presence of water, absorbs oxygen from the air, and is converted into sulphate, which may then be extracted by water.

Iron vitriol has an extended practical application; among other uses, it is employed in the preparation of ink, and in dyeing.

When heated it decomposes according to the following equation:—

$$2FeSO_4 = Fe_2O_3 + SO_3 + SO_2.$$

On this is based the production of fuming Nordhausen sulphuric acid (p. 198), and of colcothar.

Ferrous Carbonate—$FeCO_3$—exists in nature as siderite, crystallized in yellow-colored rhombohedra, isomorphous with calcite and smithsonite. Sodium carbonate added to ferrous solutions precipitates a white voluminous carbonate, which rapidly oxidizes in the air to ferric hydroxide. Ferrous carbonate is somewhat soluble in water containing carbon dioxide, hence present in many natural waters.

Ferrous Phosphate—$Fe_3(PO_4)_2 + 8H_2O$—occurs crystallized in bluish monoclinic prisms as *Vivianite.* Precipitated by sodium phosphate from ferrous solutions, it is a white amorphous powder, which oxidizes in the air.

Ferrous Sulphide—FeS—is a dark-gray, metallic mass, obtained by fusing together iron and sulphur. It is made use of in laboratories for the preparation of hydrogen sulphide. If an intimate mixture of iron filings and sulphur be moistened with water, the union will occur even at ordinary temperatures. Black ferrous sulphide is precipitated from ferrous solutions by alkaline sulphides. When the moist sulphide is exposed to the air it oxidizes to ferrous sulphate. The alkaline sulphides also precipitate ferrous sulphide from ferric salts, but the latter first suffer reduction:—

$$Fe_2Cl_6 + (NH_4)_2S = 2FeCl_2 + 2NH_4Cl + S,$$

and

$$FeCl_2 + (NH_4)_2S = FeS + 2NH_4Cl.$$

FERRIC COMPOUNDS.

Ferric Oxide—*Sesquioxide of Iron*—Fe_2O_3—exists in nature, in compact masses, as hematite, and as iron mica, in dark-gray metallic rhombic prisms. It may be prepared by heating the iron oxygen compounds in the air, and is obtained on a large scale by the ignition of green vitriol. It is then a dark-red powder (*colcothar* or *caput mortuum*) used as a paint and for polishing glass.

Ferric Hydroxide—$Fe_2(OH)_6$—is precipitated by alkalies from ferric solutions as a voluminous, reddish-brown mass. On boiling, it becomes more compact, gives up water, and is converted into the hydrate, $Fe_2O(OH)_4$. Many iron ores, like bog-iron ore, $Fe_2O(OH)_4$, pyrosiderite, $Fe_2O_2(OH)_2$ (isomorphous with diaspore), and brown hematite $Fe_4O_3(OH)_6$, are derived in a similar manner.

Freshly precipitated ferric hydroxide is soluble in a solution of ferric chloride or acetate. When such a solution is subjected to dialysis, the iron salt diffuses, and there remains a pure aqueous solution of ferric hydroxide. All of the latter is precipitated as a jelly from such a solution upon the addition of a little alkali or acid.

Ferrous-Ferric Oxide—$Fe_3O_4 = FeO.Fe_2O_3$—occurs in nature crystallized in black regular octahedra—magnetite. It is abundant in Sweden, Norway, and the Urals. It may be obtained artificially by conducting steam over ignited iron (p. 400). Magnetite constitutes the natural magnets.

Ferric hydroxide, like other sesquioxides, is a feeble base, and does not yield salts with weak acids, like carbonic or sulphurous (p. 355).

Ferric salts arise by the solution of ferric oxide in acids, or by the oxidation of ferrous salts in the presence of free acids (best by chloric or nitric acids):—

$$2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O.$$

They generally have a yellow-brown color, and are converted by reduction into ferrous salts:—

$$Fe_2Cl_6 + H_2S = 2\,FeCl_2 + 2HCl + S.$$

Ferric Chloride—Fe_2Cl_6.—It is obtained in aqueous solution by conducting chlorine into a solution of ferrous chloride:—

$$2FeCl_2 + Cl_2 = Fe_2Cl_6.$$

The hydrate—$Fe_2Cl_6 + 6H_2O$—remains upon evaporation. It is a yellow crystalline mass, readily soluble in water, alcohol, and ether. It is partially decomposed when heated; hydrogen chloride escapes, and a mixture of chloride and oxide remains.

Anhydrous ferric chloride is produced by heating iron in a current of chlorine gas; it sublimes in brownish-green, metallic, shining, six-sided prisms and scales, which deliquesce in the air. The specific gravity of their vapor at 440° closely approximates the formula Fe_2Cl_6 (found 10.5; calculated 11.2); with rising temperature it diminishes successively and from 750–1050° corresponds to the simple formula $FeCl_3$. At still higher temperatures a partial decomposition occurs into ferrous chloride and chlorine (Grünewald and v. Meyer).

Ferric Sulphate—$Fe_2(SO_4)_3$—is obtained by dissolving the oxide in sulphuric acid. When its solution is evaporated, it remains as a white mass, which gradually dissolves in water, with a reddish-brown color. It forms alums (p. 350) with alkaline sulphates, *e.g.*:—

$$Fe_2(SO_4)_3 . K_2SO_4 + 24H_2O.$$

Potassium iron alum.

Ferric Phosphate—$Fe_2(PO_4)_2$—is a white precipitate, thrown out of ferric solutions by sodium phosphate. It is insoluble in water and acetic acid.

Ferric Sulphide—FeS_2—occurs in nature as *pyrites*, crystallized in yellow, metallic, shining, regular cubes or octahedra. It is employed in the manufacture of sulphuric acid and green vitriol. The artificial sulphide can be prepared in many ways.

COMPOUNDS OF FERRIC ACID.

On fusing iron filings with nitre, or by conducting chlorine into potassium hydroxide, in which ferric hydroxide is suspended, *Potassium Ferrate*, K_2FeO_4, is produced, and crystallizes from the alkaline solution in dark-red prisms. This salt is isomorphous with potassium chromate and sulphate. It dissolves quite easily in water; but the dark-red liquid soon decomposes with separation of ferric hydroxide and oxygen. The free acid is not known, as it immediately breaks up when liberated from its salts.

CYANOGEN DERIVATIVES OF IRON.

Iron unites with the cyanogen group to form compounds which are very characteristic, and important in a commercial sense. When potassium cyanide is added to aqueous solutions of the ferrous or ferric salts, the cyanides, $Fe(CN)_2$ and $Fe_2(CN)_6$, are thrown down as white precipitates, but decompose rapidly in the air. They dissolve in an excess of potassium cyanide to form the double cyanides, $Fe(CN)_2.4KCN$ and $Fe_2(CN)_6.6KCN$. When acids are added to these solutions the hydrogen compounds, H_4FeCy_6*(= $FeCy_2.4HCy$) and $Fe_6Cy_{12}H_6$(= $Fe_2Cy_6.6HCy$) separate.

These are of acid nature, and form salts by exchanging their hydrogen for metals. The iron and the cyanogen group in these

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* The cyanogen group, CN, is usually designated by the letters Cy.

salts and the free acids cannot be detected by the usual reagents (*e.g.*, the iron is not precipitated by the alkalies). It is supposed that compound groups of peculiar structure are present in these double cyanides, and that they conduct themselves like the halogens. The group, $FeCy_6$, in the *ous* compounds is called *ferrocyanogen*, that of Fe_2Cy_{12} in the *ic*, *ferricyanogen*. The ferro- behave toward the ferri-compounds the same as the ferrous toward the ferric salts; oxidizing agents convert the former into the latter, and reducing agents transform the latter into the former:—

$$2FeCy_6K_4 + Cl_2 = K_6Fe_2Cy_{12} + 2KCl$$

and

$$Fe_2Cy_{12}K_6 + 2KOH + H_2 = 2K_4FeCy_6 + 2H_2O.$$

Cobalt, manganese, chromium and the platinum metals afford similar cyanides.

Potassium Ferrocyanide—*Yellow Prussiate of Potash*—K_4FeCy_6, is produced by the action of potassium cyanide upon iron compounds, or upon free iron (in which case the oxygen of the air or water takes part). It is prepared commercially by igniting carbonized nitrogenous animal matter (blood, horns, hoofs, leather offal, etc.) with potashes and iron.

In this operation, the carbon and nitrogen of the organic matter combine with the potassium of the potashes to form potassium cyanide, while the sulphur present forms iron sulphide with the iron. (By means of alcohol, potassium cyanide can be extracted from the fusion.) Upon treating the fusion with water, the potassium and iron sulphide react upon each other, and ferrocyanide of potassium results and is purified by crystallization:—

$$FeS + 6KCy = K_4FeCy_6 + K_2S.$$

It crystallizes from water in large, yellow, monoclinic prisms, having three molecules of water, and soluble in 3–4 parts H_2O. The crystals lose all their water at 100°, and are converted into a white powder. At a red heat the ferrocyanide breaks up into potassium cyanide, nitrogen, and iron carbide (FeC_2). When the salt is warmed with dilute sulphuric acid, half of the cyanogen escapes as hydrogen cyanide; concentrated sulphuric acid decomposes it, according to the following equation:—

$$K_4FeCy_6 + 6H_2SO_4 + 6H_2O = FeSO_4 + 2K_2SO_4 + 3SO_4(NH_4)_2 + 6CO.$$

When strong hydrochloric acid is added to a concentrated solution of potassium ferrocyanide *hydrogen ferrocyanide*, H_4FeCy_6, separates as a white crystalline powder, which soon turns blue in the air. It has the nature of an acid. Its salts with the alkali and alkaline earth metals are very soluble in water. The sodium salt crystallizes with difficulty. The salts of the heavy metals are insoluble, and are obtained by double decomposition. When potassium ferrocyanide is added to the solution of a ferric salt a dark-blue cyanide $(FeCy_6)_3(Fe_2)_2$, called *Prussian Blue* is precipitated:—

$$3K_4FeCy_6 + 2Fe_2Cl_6 = (FeCy_6)_3(Fe_2)_2 + 12KCl.$$

This is the ferric salt of hydroferrocyanic acid; and if potassium or sodium hydroxide is poured over it, it is converted into ferrocyanide of potassium and ferric hydroxide:—

$$(FeCy_6)_3(\overset{VI}{Fe_2})_2 + 12KOH = 3K_4FeCy_6 + 2\overset{VI}{Fe_2}(OH)_6.$$

Potassium ferrocyanide produces a reddish-brown precipitate of $FeCy_6Cu_2$ in copper solutions.

Oxidizing agents convert the ferro- into **potassium ferricyanide**—$K_6Fe_2Cy_{12}$—*red prussiate of potash.* This conversion is most conveniently effected by conducting chlorine into the solution of the yellow prussiate:—

$$2K_4FeCy_6 + Cl_2 = K_6Fe_2Cy_{12} + 2KCl.$$

The ferrocyanogen group, $FeCy_6$, is then changed to the ferri-, $Fe_2Cy^1_2$ (p. 404).

The red prussiate crystallizes from water in red rhombic prisms. The free hydroferricyanic acid, $H_6Fe_2Cy_{12}$, is precipitated upon the addition of concentrated hydrochloric acid. It is rather unstable.

With ferrous solutions potassium ferricyanide affords a dark-blue precipitate, $Fe_3Fe_2Cy_{12}$, very similar to Prussian Blue, and called *Turnbull's Blue*:—

$$K_6Fe_2Cy_{12} + 3FeSO_4 = Fe_2Cy_{12}\overset{II}{Fe_3} + 3K_2SO_4.$$

This blue is the ferrous salt of hydroferricyanic acid. Alkalies convert it into ferricyanide of potassium and ferrous hydroxide:—

$$Fe_2Cy_{12}Fe_3 + 6KOH = Fe_2Cy_{12}K_6 + 3Fe(OH)_2.^*$$

Potassium ferricyanide does not cause precipitation in ferric solutions. Ferrocyanide yields Prussian blue, while it forms a bluish white precipitate in ferrous solutions.

By these reactions, ferric salts may be readily distinguished from

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[*] According to recent investigations it appears that Turnbull's blue and Prussian blue possess the same composition $(FeCy_6)_2 \left\{ \begin{matrix} \overset{VI}{Fe_2} \\ Fe \end{matrix} \right.$. The simpler relations are retained here.

the ferrous. Potassium sulphocyanide (CNSK) produces a dark-red coloration in ferric solutions, while it leaves the ferrous unaltered.

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2. COBALT.

Co = 58.6.

Occurs in nature as smaltite ($CoAs_2$) and cobaltite ($CoAs_2.CoS_2$). The metal is obtained by the ignition of cobaltous oxide with carbon, or in a current of hydrogen. It has a reddish-white color and strong lustre, is very tenacious, and fuses with difficulty. Its specific gravity is 8.9. It is attracted by magnets, but to a less degree than iron. It is not altered by the air or water. It is only slightly attacked by hydrochloric and sulphuric acids; nitric acid dissolves it readily, forming cobaltous nitrate.

The predominating compounds have the form CoX_2, and are called *cobaltous*. They are very stable, and generally isomorphous with the ferrous salts. The hydrous cobaltous compounds have a reddish color, the anhydrous are blue.

COBALTOUS COMPOUNDS.

Cobaltous Chloride—$CoCl_2$—is obtained by the solution of cobaltous oxide in hydrochloric acid, and crystallizes with $6H_2O$ in red monoclinic prisms. When heated, it loses water, and becomes anhydrous and blue in color. Characters made with this solution upon paper are almost invisible, but when warmed they become distinct and blue (sympathetic ink).

Cobaltous Hydroxide—$Co(OH)_2$—is a reddish precipitate produced by the alkalies in hot, cobaltous solutions. When exposed to the air, it browns by oxidation. Basic salts are precipitated from cold solutions. When heated out of air contact, the hydroxide passes into green *cobaltous oxide*, CoO.

Cobaltous Sulphate—$SO_4Co + 7H_2O$—crystallizes in dark-red monoclinic prisms; the hydrated sulphate, $CoSO_4 + 6H_2O$, separates from hot solutions. It is isomorphous with ferrous sulphate, and yields double salts with alkaline sulphates.

Cobaltous Nitrate—$Co(NO_3)_2 + 6H_2O$—forms red deliquescent prisms.

Cobaltous Sulphide—CoS—is a black precipitate, produced in neutral cobalt solutions by alkaline sulphides. It is insoluble in dilute acids.

Cobalt Silicates.—When glass is fused with a cobalt compound it is colored a dark blue, and when reduced to a powder is used as a paint, under the name of *smalt*.

Smalt is prepared commercially by fusing cobalt ores with potashes and quartz. The cobalt forms a silicate (smalt) with the SiO_2 and potassium, while the other metals accompanying it in its ores, such as Bi, As, and especially nickel, are thrown out as a speiss. This is called speiss-cobalt and serves for the preparation of nickel.

On igniting cobalt oxide, Co_2O_3, with alumina, a dark-blue mass is produced—*cobalt ultramarine* or *Thenard's Blue*. When zinc oxide and cobalt oxide are ignited a green color—*green cinnabar* or *Rinman's Green*—is obtained.

COBALTIC COMPOUNDS.

Cobaltic Oxide—Co_2O_3—is left as a black powder on the ignition of cobaltous nitrate. It becomes cobaltous-cobaltic oxide, Co_3O_4, at a red heat, and cobaltous oxide at a white heat. The hydroxide—$Co_2(OH)_6$—separates as a dark-brown powder, if chlorine be passed through an alkaline solution containing a cobaltous salt.

A cobaltous salt is produced, and oxygen set free, when sulphuric acid acts upon the oxide or the hydroxide. Chlorine is generated when it is heated with hydrochloric acid :—

$$Co_2O_3 + 6HCl = 2CoCl_2 + 3H_2O + Cl_2.$$

The cobaltic hydroxide dissolves in dilute, cold hydrochloric acid, with scarcely any liberation of chlorine; the solution probably contains Co_2Cl_6, which decomposes into $2CoCl_2$ and Cl_2 on evaporation.

Cobaltous-Cobaltic Oxide — $Co_3O_4 = Co_2O_3.CoO$—corresponding to magnetite, Fe_3O_4, is formed upon the ignition of the oxygen cobalt derivatives, and is a black powder.

Only a few salts of cobalt in the *ic* state are known. The most interesting of these is **potassio-cobaltic nitrite.**

When potassium nitrite, KNO_2, is added to a cobaltous solution acidified with acetic acid, nitrogen is set free, and in course of time $Co_2(NO_2)_6.6KNO_2 + nH_2O$, the double salt, separates as a yellow crystalline powder. This reaction is very characteristic for cobalt, and serves to separate it from nickel.

Ammonio-Cobalt Compounds.—Cobalt is capable of forming a series of peculiar compounds with ammonia, in which the metal appears in its highest state of oxidation; the structure of these derivatives has not yet been explained. On adding ammonium hydroxide to a cobaltous chloride solution, the precipitate first formed dissolves in the excess of the reagent, and when this liquid is permitted to stand exposed to the air, the color, which is brown at first, gradually passes into red. On adding concentrated hydrochloric acid to this solution, a brick-red, crystalline powder, of the composition—$Co_2Cl_6.10NH_3 + 2H_2O$—called *roseoco-*

baltic chloride—is precipitated. If, however, the red solution be boiled with hydrochloric acid, a red powder—*purpureocobaltic chloride*, $Co_2Cl_6.10NH_3$—separates out. If the ammoniacal red solution contain much ammonium chloride, hydrochloric acid will precipitate a yellowish-brown compound—*luteocobaltic chloride*, $Co_2Cl_6.12NH_3$.

The other salts of cobalt, such as the sulphate and nitrate, yield similar compounds, *e.g.*, $Co_2(NO_3)_6.10NH_3$, *roseocobaltic nitrate.*

Cyanogen Cobalt Compounds.—In solutions of cobaltous salts, potassium cyanide produces a bright brown precipitate of *cobalto-cyanide* $Co(CN)_2$, soluble in an excess of the reagent. The solution absorbs oxygen from the air, and is converted into *potassium cobalticyanide*, $K_6Co_2(CN)_{12}$, corresponding to potassium ferricyanide. When the solution is evaporated the cobalticyanide crystallizes in colorless rhombic prisms, very soluble in water. Sulphuric acid precipitates *hydrogen cobalticyanide*, $H_6Co_2(CN)_{12}$, from the concentrated solution. This acid crystallizes in needles.

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3. NICKEL.

$Ni = 58.6$.

Nickel exists in native condition in meteorites; its most important ores are *Niccolite*—NiAs—and *Gersdorffite*, $NiS_2.NiAs_2$ (constituted like cobaltite). It is always accompanied in its ores by cobalt, and *vice versâ,* cobalt usually by nickel. The isolation of the latter from its ores and from speiss cobalt (p. 407) is very complicated. Nickel usually appears in commerce in cubical forms, which in addition to the chief ingredient always contain some copper, bismuth, and other metals. Chemically pure nickel is procured by igniting the oxalate or carbonate in a current of hydrogen. Nickel is almost silver-white in color and is very lustrous, and very tenacious. Its specific gravity is 9.1, and that of the fused variety 8.8. It fuses at a somewhat lower temperature than iron, and like it is attracted by the magnet. It is not altered in the air; it dissolves with difficulty in hydrochloric and sulphuric acids, but readily in nitric acid.

Nickel, like iron, also combines with carbon monoxide, yielding the liquid compound $Ni(CO)_4$, boiling at 43°, and solidifying at —25° to needle-shaped crystals. At 60° the vapor of the liquid explodes with violence (*Chem. Jour.*, 57, 749). Nickel can be perfectly separated from cobalt by means of this derivative.

Its derivatives are almost exclusively of the *ous* form NiX_2; nickelic oxide behaves like a peroxide, and does not afford corresponding salts.

Nickelous Hydroxide—$Ni(OH)_2$—is a bright-green precipitate produced by alkalies in nickelous solutions. It dissolves in ammonium hydroxide, with a blue color. When heated it passes into gray nickelous oxide, NiO.

Nickelous Chloride—$NiCl_2 + 6H_2O$—consists of green, monoclinic prisms. When heated they lose water and become yellow.

Nickelous Cyanide—$Ni(CN)_2$—is precipitated by potassium cyanide as a green-colored mass from nickel solutions. It is soluble in excess of the precipitant. The double cyanide, $NiCy_2.2KCy + H_2O$, crystallizes from the solution. This salt is readily decomposed by acids. Cyanogen compounds of nickel, constituted like those of iron and cobalt, are not known.

Nickelous Sulphate—$NiSO_4 + 7H_2O$—appears in green, rhombic prisms, isomorphous with the sulphates of the magnesium group, and forms analogous double salts.

Nickelous Sulphide—NiS—is precipitated, black in color, by alkaline sulphides from nickel solutions.

Nickelic Oxide—Ni_2O_3—and **Hydroxide**—$Ni_2(OH)_6$—are perfectly similar to the corresponding cobalt salts; when warmed with hydrochloric acid they liberate chlorine.

Nickel is used for certain alloys. Argentan consists, ordinarily, of 50 per cent. copper, 25 per cent. nickel and 25 per cent. zinc. The German nickel coins consist of 75 per cent. Cu and 25 per cent. Ni. The alloy will be whiter in color and harder, and also receive a higher polish in proportion to the amount of nickel that it contains. At present, cast-iron ware is coated with a layer of nickel to prevent it from rusting and to impart to it a beautiful white surface. This is accomplished in an electrolytic manner, or by boiling the iron ware in a solution of zinc chloride and nickel sulphate.

In the electrolytic method the solution of the double sulphate of nickel and ammonium is employed; the positive electrode consists of a pure nickel plate, while the object to be coated is attached to the negative electrode.

GROUP OF THE PLATINUM METALS.

Besides platinum, this group comprises palladium, rhodium, ruthenium, osmium and iridium—the constant companions of the first in its ores. On page 395 we observed that these metals are divided into two groups; the *group of light platinum metals*, and the *group of heavy platinum metals* which have higher atomic weights and specific gravities:—

	Ru, 101.7	Rh, 103	Pd, 106	Os, 192	Ir, 193.2	Pt, 194.8
Sp. gr.	" 12.26	" 12.1	" 11.8	" 22.4	" 22.38	" 21.4

The relations of the metals of this group to each other are perfectly similar to those of the iron group; and they show in their physical and chemical properties a great resemblance to the corresponding members of the iron group. Osmium and ruthenium, like iron, have a gray color, fuse with difficulty and are readily oxidized in the air. Palladium and platinum, on the other hand, have an almost silver-white color like nickel, are more fusible, and are not oxidized by oxygen. In chemical respects osmium and ruthenium, like iron, also show a metalloidal nature, inasmuch as their highest oxygen compounds form acids. Their derivatives show a complete parallelism with those of iron :—

II	III	IV	VI
OsO	Os_2O_3	OsO_2	(OsO_3)
Osmous oxide.	Osmic oxide.	Osmium dioxide.	Osmic trioxide.
RuO	Ru_2O_3	RuO_2	(RuO_3)
Ruthenous oxide.	Ruthenic oxide.	Ruthenium dioxide.	Ruthenium trioxide.

The acid oxides OsO_3 and RuO_3 are unknown, but the corresponding acids, H_2OsO_4 (osmic acid) and H_2RuO_4 (ruthenic acid), and their salts have been obtained. Besides the derivatives already mentioned we find that osmium and ruthenium are capable of still higher oxidation, yielding OsO_4, per-osmic oxide, and RuO_4, per-ruthenic oxide—which is not the case with iron; in these compounds the metals appear to be octads, yet these oxides do not afford corresponding acids or salts.

Rhodium and iridium, like cobalt, do not yield acid-like derivatives. Their salts correspond to the forms:—

II	III	IV
RhO	Rh_2O_3	RhO_2.
Rhodous oxide.	Rhodic oxide.	Rhodium dioxide.

The rhodic compounds are the more stable.

Palladium and platinum, finally, are relatively of more basic nature, as their *ous* derivatives, PdX_2 and PtX_2, are proportionally more stable than the *ic* forms, PdX_4 and PtX_4. Palladium also forms a lower oxide, palladium suboxide, Pd_2O, in which it approaches silver.

The platinum metals are found in nature almost exclusively in the so-called platinum ore, which usually occurs in small metallic grains in accumulated sands of a few regions (in California, Australia, the Island of Sumatra, and especially in the Urals). The platinum ore, like that of gold, is obtained by the elutriation of the platiniferous sand with water whereby the lighter particles are carried away. Platinum ore usually contains 50–80 per cent. platinum, besides palladium (to 2 per cent,), iridium (to 7 per cent.), osmium (1½ per cent.), and ruthenium (1½ per cent.), and different other metals, as gold, copper, and iron.

The separation of the platinum metals is generally executed in the following manner: The gold is first removed by dilute aqua regia. Then the ore is treated with concentrated aqua regia, when platinum, palladium, rhodium, ruthenium, and a portion of iridium are dissolved. Metallic grains or leaflets, an alloy of osmium and iridium—platinum residues—remain. Ammonium chloride is then added to the solution and platinum and iridium precipitated as double salts. When the precipitate is ignited, a spongy mass of iridium-bearing platinum (platinum sponge) is obtained, which is applied directly in the manufacture of platinum vessels. The filtered solution from the insoluble chlorides contains palladium, rhodium, and ruthenium, which are thrown down as a metallic powder by iron; their further separation is then effected in various ways.

Formerly spongy platinum was employed almost exclusively for the manufacture of platinum objects; it was pressed into moulds, then ignited and hammered out. Now the fusibility of Pt in the oxy-hydrogen flame is resorted to, and the fused metal run into moulds.

Platinum containing both iridium and rhodium may be fused directly out of the platinum-ore by means of the oxy-hydrogen blowpipe. The greater portion of the osmium and ruthenium is consumed in this operation. The presence of iridium and rhodium makes platinum harder and less readily attacked by many reagents.

RUTHENIUM AND OSMIUM.

Ru = 101.7. Os = 192.

Ruthenium has a steel-gray color; it is very hard, brittle, and difficultly fusible (about 1800°). When pulverized and ignited in the air it oxidizes to RuO and Ru_2O_3. It is insoluble in acids, and only slowly dissolved by aqua regia. When fused with potassium hydroxide and nitrate, it forms potassium rutheniate, K_2RuO_4.

Ruthenium heated in chlorine gas yields *ruthenium dichloride*, $RuCl_2$, a black powder, insoluble in acids. The *sesquichloride*, Ru_2Cl_6, is obtained by the solution of $Ru_2(OH)_6$ in hydrochloric acid, and is a yellow, crystalline mass, which deliquesces in the air. It yields crystalline double chlorides with potassium and ammonium chlorides, *e.g.*, $Ru_2Cl_6 \cdot 4KCl$. The *tetrachloride*, $RuCl_4$, is only known in double salts. *Ruthenious oxide*, RuO, the *sesquioxide*, Ru_2O_3, and *dioxide*, RuO_2, are black powders, insoluble in acids, and are obtained when ruthenium is roasted in the air.

The *hydroxides*, $Ru_2(OH)_6$ and $Ru(OH)_4$, are produced by the action of the alkalies upon the corresponding chlorides, and are very readily soluble in acids. *Ruthenic acid*, H_2RuO_4, is not known in a free condition. Its potassium salt,

K_2RuO_4, is formed by fusing the metal with potassium hydroxide and nitre. It dissolves in water with an orange-yellow color. When chlorine is conducted through the solution *ruthenium tetroxide*, RuO_4, separates as a gold-yellow crystalline mass. It fuses at 40°, boils about 100°, and yields a yellow vapor, the odor of which is similar to nitrogen dioxide, NO_2. It decomposes with explosion at 108°. Water breaks it up with formation of $Ru_2(OH)_6$. It dissolves to RuO_4K_2 in concentrated potassium hydroxide. When less chlorine is introduced into the solution of RuO_4K_2, greenish-black crystals separate out, which are isomorphous with potassium permanganate, and appear to be RuO_4K.

Osmium is very much like the preceding. It is not even fusible in the oxyhydrogen flame; it only sinters together. According to Violle it fuses at 2500°. Reduced to a fine powder it will burn when ignited in the air to OsO_4. Nitric acid and aqua regia convert it into the same oxide. The compounds, $OsCl_2$ and OsO, Os_2Cl_6 and Os_2O_3,OsO_2 and $OsCl_4$, are very similar to the corresponding ruthenium derivatives. By fusion with potassium hydroxide and nitre we get *potassium osmate*—K_2OsO_4—which crystallizes from aqueous solution with $2H_2O$ in dark-violet octahedra. The most stable and a very characteristic derivative of osmium is the *tetroxide*, OsO_4, which is produced by igniting the metal in the air, or by the action of chlorine on osmium in the presence of water. It crystallizes in large colorless prisms, which fuse below 100° and distil at a somewhat higher temperature. It has a very sharp, piercing odor, similar to that of sulphur chloride. Reducing and organic substances precipitate pulverulent osmium from it. This is the basis of its application in microscopy.

OsO_4 and RuO_4 do not afford corresponding salts.

RHODIUM AND IRIDIUM.

Rh = 103. Ir = 193.2.

These metals are lighter in color and are more easily fusible than ruthenium and osmium. (Iridium fuses at 1950°.) When pure they are not attacked by acids or aqua regia; but dissolve in the latter when alloyed with platinum.

Rhodium forms three oxides: RhO, Rh_2O_3 and RhO_2, of which the second forms salts with acids. RhO_2 results when rhodium is heated with nitre.

Of the chlorides only Rh_2Cl_6 is known. It results when the metal is heated in chlorine gas. It is a brownish-red mass. It forms readily crystallizing, red-colored double salts with alkaline chlorides.

Iridium has perfectly analogous derivatives: IrO, Ir_2O_3, IrO_2, and $IrCl_2$, Ir_2Cl_6, $IrCl_4$. The *sesquichloride*, Ir_2Cl_6, formed by heating Ir in chlorine, is an olive-green, crystalline mass, insoluble in water and acids. It affords double salts with the alkaline chlorides, *e.g.*, $Ir_2Cl_6.6KCl + 6H_2O$, which crystallizes from water in green crystals. They are also produced by the action of SO_2 upon the double salts of $IrCl_4$.

Iridium Tetrachloride—$IrCl_4$—is produced in the solution of iridium or its oxide in aqua regia, and remains, on evaporation, as a black mass, readily soluble in water (with red color). When alkaline chlorides are added to the solution double chlorides are precipitated, *e. g.*, $IrCl_4.2NH_4Cl$, isomorphous with the double chlorides of platinum. When a solution of $IrCl_4$ is boiled with KOH, $Ir(OH)_4$ will be precipitated.

PALLADIUM.

Pd = 106.

Palladium, in addition to occurring in platinum ores, is found alloyed with gold (Brazil), and in some selenium ores (Hartz); it has a silver-white color, and is somewhat more fusible (about 1500°) than platinum. When finely divided it dissolves in boiling concentrated hydrochloric, sulphuric, and nitric acids. When ignited in the air it at first becomes dull by oxidation, but at a higher temperature the surface again assumes a metallic appearance.

Palladium absorbs hydrogen gas (occlusion) to a much greater extent than platinum or silver. Freshly ignited palladium leaf absorbs upwards of 370 volumes of hydrogen at ordinary temperatures, and about 650 volumes at 90–100° C. A greater absorption may be effected at ordinary temperatures in the following manner:—

Water is decomposed by the electric current, palladium foil being used as a negative electrode. The liberated hydrogen is then taken up by the palladium (to 960 volumes); the metal expands ($\frac{1}{10}$ its volume), becomes specifically lighter, but retains its metallic appearance entire. According to the investigations of Debray, the compound Pd_2H is produced, which contains dissolved hydrogen, and deports itself similarly to an alloy (compare p. 47). Palladium charged with hydrogen usually remains unaltered in the air, and in a vacuum; it, however, sometimes becomes heated in the air, as the hydrogen is oxidized to water. The same occurs when palladium hydride is heated to 100°; *in vacuo*, all the hydrogen escapes as gas. Palladium hydride is a strong reducing agent, like nascent hydrogen. Ferric salts are reduced to the ferrous state; chlorine and iodine in aqueous solution are converted into hydrochloric and hydriodic acids.

Palladium black absorbs hydrogen more energetically than the compact variety (at 100° upwards of 980 volumes). This substance is obtained by the reduction or electrolysis of palladic chloride. If palladium sponge be heated in the air until the white metallic color becomes black, in consequence of the superficial oxidation, it will absorb hydrogen very energetically at ordinary temperatures, and partially oxidize it to water.

When palladium-sheet or sponge is introduced into the flame of a spirit-lamp, it is covered with smoke; this is due to the fact that the metal withdraws the hydrogen of the hydrocarbons, and carbon is set free.

There are two series of palladium compounds: the *palladious*, PdX_2, and *palladic*, PdX_4. The first are well characterized and are distinguished by their stability.

Palladious Chloride—$PdCl_2$—remains as a brown, deliquescent mass, on evaporating the solution of palladium in aqua regia. It yields easily soluble crystalline double salts, with alkaline chlorides, *e.g.*, $PdCl_2.2KCl$.

Palladious Iodide—PdI_2—is precipitated from palladium solutions by potassium iodide as a black mass, insoluble in water.

Palladious Oxide—PdO—is a black residue left upon careful ignition of the nitrate. It is difficultly soluble in acids. When heated, it loses oxygen, and forms *palladium suboxide*, Pd_2O.

When palladium is dissolved in sulphuric or nitric acids, the corresponding salts are produced.

The **sulphate**, $PdSO_4 + 2H_2O$, is composed of brown crystals, readily soluble in water. Much of the latter decomposes it.

Palladic Chloride—$PdCl_4$—is formed when the metal is dissolved in aqua regia. It decomposes, on evaporation, into $PdCl_2$ and Cl_2. When potassium or ammonium chloride is added to its solution, red-colored, difficultly soluble double chlorides crystallize out; they are analogous to the corresponding salts of platinum.

PLATINUM.

Pt = 194.8.

The separation of platinum from the ore was described on page 411. The metal has a grayish-white color, and a specific gravity of 21.4. It is very tough and malleable, and may be drawn out into very fine wire and rolled into foil. It becomes soft without melting at an intense heat. It fuses in the oxy-hydrogen flame (about 1770°—Violle), and is somewhat volatile. On fusion, it absorbs oxygen, which it gives up again on cooling (like silver). At ordinary temperatures, it also condenses oxygen upon its surface, especially when in a finely divided state, as *platinum black* or *sponge*. The first is obtained, if reducing substances, like zinc, be added to solutions of platinic chloride or upon boiling the solution with sugar and sodium carbonate; it absorbs as much as 250 volumes of oxygen. Platinum sponge is obtained by the ignition of $PtCl_4$-$2NH_4Cl$. The production of various reactions is due to this power of platinum to condense oxygen; thus hydrogen will inflame in the air, if it be conducted upon platinum sponge; sulphur dioxide combines with O at 100° to form the trioxide. At a red heat platinum permits free passage to hydrogen, while it is not permeable by oxygen and other gases (p. 265).

Platinum is not attacked by acids; it is only soluble in liquids generating free chlorine, *e.g.*, aqua regia. In consequence of this resistance to acids, and its unalterability upon ignition, this metal answers as an undecomposable material for the production of chemical crucibles, dishes, wire, etc. The usual presence of iridium in ordinary platinum increases its durability.

The alkaline hydroxides, sulphides, and cyanides attack it strongly at a red heat. It forms readily fusible alloys with phosphorus, arsenic, and many heavy metals, especially lead, and many heavy metals are reduced from their salts by platinum. Therefore such substances must not be ignited in platinum crucibles, etc.

Platinum, like palladium, affords *platinous*, PtX_2, and *platinic*, PtX_4, derivatives; in the first it is more basic, in the latter more acidic.

Platinic Chloride—$PtCl_4$—is obtained by the solution of platinum in aqua regia, and when the liquid is evaporated with an excess of hydrochloric acid, hydrogen chloroplatinate, $PtCl_4.2HCl = H_2PtCl_6$, crystallizes with six molecules of water in brownish red, deliquescent prisms. It forms characteristic double chlorides, $PtCl_4.2KCl$, with ammonium and potassium chloride. These are difficultly soluble in water; hence, on mixing the solutions, they immediately separate out as a crystalline yellow powder. Ignition completely decomposes the ammonium salt, leaving spongy platinum.

Platinum chloride affords similar insoluble double chlorides with those of rubidium, cæsium, and thallium, while that with sodium, $PtCl_6Na_2 + 6H_2O$, is very soluble in water.

On adding NaOH to platinic chloride and then supersaturating with acetic acid, there separates a reddish-brown precipitate of *platinic hydroxide*, $Pt(OH)_4$. This dissolves readily in acids (excepting acetic), with formation of salts. The oxygen salts, as $Pt(SO_4)_2$, are very unstable. The hydroxide has also an acidic character (*platinic acid*), and dissolves in alkalies, yielding salts with them. These, also, result on fusing platinum with potassium and sodium hydroxide. The barium salt, $Pt\left\{\begin{matrix}(OH)_2\\O_2Ba\end{matrix}\right. + 3H_2O$, is precipitated from platinic chloride, by barium hydroxide, as a yellow, crystalline compound. The acidic nature of its hydroxide allies platinum to gold. If hydrogen sulphide be conducted through platinic solutions, black *platinum disulphide*, PtS_2, is precipitated; it is soluble in alkaline sulphides, with formation of sulpho-salts.

Platinous Chloride—$PtCl_2$—is a green powder, insoluble in water, remaining after heating $PtCl_4$ to 200°. It affords double salts with alkaline chlorides, *e. g.*, $PtCl_2.2NaCl$. When digested with potassium hydroxide it yields the hydroxide, $Pt(OH)_2$.

Cyanogen Compounds.—Like iron and cobalt, platinum affords double cyanides corresponding to the ferrocyanides. When platinous chloride is dissolved in potassium cyanide *platinum potassium cyanide*, $K_2PtCy_4 + 3H_2O$, crystallizes on evaporation in large prisms exhibiting magnificent dichroism; in transmitted light they are yellow and in reflected light blue. This salt must be viewed as the potassium compound of *hydro-platino-cyanic acid*, H_2PtCy_4. When separated from its salts it crystallizes in gold-yellow needles. Its salts with heavy metals are obtained by double decomposition, and all show a beautiful play of colors.

Platinum-Ammonium Compounds.—There is a whole series of these, which must be viewed as platinum bases and their salts. They are constituted according to the following empirical formulas:—

$$Pt(NH_3)_2X_2, \quad Pt(NH_3)_2X_4, \quad Pt(NH_3)_4X_2, \quad Pt(NH_3)_4X_4,$$

in which X indicates various acid residues, or halogen atoms. They arise by the action of ammonium hydroxide upon platinous chloride. The bases are obtained by substituting hydroxyl groups for the acid radicals, *e.g.*, $Pt(NH_3)_4(OH)_2$. They resemble alkaline hydroxides in their chemical properties. The other platinum metals afford similar amine derivatives. The nature and chemical constitution of these interesting compounds is, however, not fully explained.

SPECTRUM ANALYSIS.*

We observed that various substances, when introduced into a non-luminous flame, imparted to it a characteristic coloration. Thus, the sodium compounds color it yellow; the potassium, violet; thallium, green; etc. The decomposition of the light thus obtained, and, indeed, of every light, by means of a prism and the study of the resulting spectrum form the basis of spectrum analysis, established in 1859 by Kirchhoff and Bunsen. Its important applications and universal use constitute one of the greatest of scientific achievements of all ages.

As we well know, every substance, solid or liquid, heated to white heat (*e. g.*, molten platinum; lime heated in the oxyhydrogen flame; the ordinary flame containing glowing particles of carbon;)

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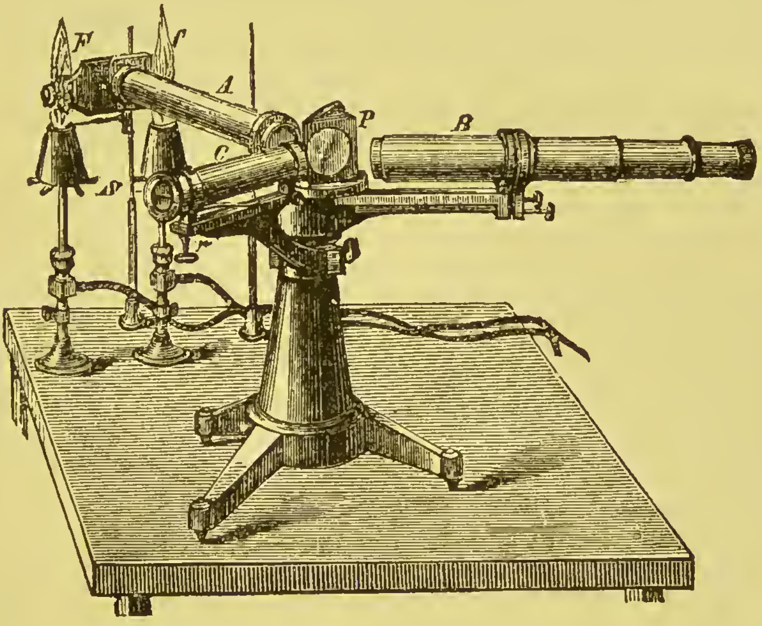
* A more exhaustive, concise, and distinct presentation of the spectrum phenomena may be found in Herman W. Vogel's "Practische Spectralanalyse irdischer Stoffe," 1888.

emits rays of every refrangibility; and hence furnishes a *continuous spectrum*, which brings to view all the colors of the rainbow, from red to violet, if the light be conducted through a prism. Glowing gases and vapors, on the contrary, whose molecules can execute unobstructed oscillations, emit light of definite refrangibility, and, therefore, afford spectra, consisting of single, bright lines. Thus, the spectrum of the yellow sodium flame is recognized as composed of one very bright yellow line, which by increased magnifying power is shown to consist of two lines lying very near each other. This reaction is so very delicate, that $\frac{1}{3000000}$ of a milligram of sodium may be detected by it. The violet potassium light affords a spectrum, consisting of a red and a blue line. The crimson strontium light shows in the spectrum several distinct red lines and a blue line. (See the spectrum plate.) Each of these lines corresponds to a definite relative position in the spectrum.

FIG. 89.



If substances affording different colors be introduced into a flame, the most intense color generally obscures the others; in the spectrum, however, each individual substance shows its peculiar bright lines, which appear simultaneously or succeed each other, according to the volatility of the various substances.

The spectrum apparatus or spectroscope, figured in Fig. 89, serves for the observation of the spectra.

In the middle of the apparatus is a flint-glass prism *P*. At the further end of the tube *A* is a movable vertical slit, in front of which is placed the light to be investigated. The entering light rays are directed by a collecting lens into the tube *A*, upon the prism, and the refracted rays (the spectrum) are observed by the telescope *B*. The tube *C* is employed to ascertain the relative position of the spectrum lines. This is provided at its outer end with a transparent horizontal scale. When a luminous flame is placed before the scale its divisions are reflected from the prism surface and thrown into the telescope *B*. We then see the spectrum to be studied and the scale divisions in *B* at the same time, and can readily determine the relative position of the lines of the spectrum. To study two spectra at the same time, and compare them, a three-sided, right-angled glass prism is attached in front of one-half (the lower or upper) of the slit of the tube *A*; this directs the rays of a light placed at the side (*f*, Fig. 89) through *A* upon the prism *P*. By means of *B*, two horizontal spectra will be observed, one above the other, and between are the bright divisions of the scale.

Adjustment of the Spectroscope.—To observe the spectra in the apparatus described, it is necessary to first adjust the same correctly. The tube *A* contains, besides the slit, also a lens (Collimator Lens), which serves to render parallel the bunch of rays proceeding from the slit; hence, the latter must be accurately placed in the focus of the lens. This is best accomplished as follows: The telescope (*B*) is drawn out and adjusted for some distant object, that it may be adapted for the reception of parallel rays; it is then replaced in the stand, pointed toward the slit, illuminated by a sodium chloride flame, and the slit then removed far enough to appear perfectly distinct in the telescope. To have the spectrum lines sharply defined, the slit must be made quite narrow; for feebly luminous lines it must, however, be widened. The horizontal black lines that appear in the spectrum arise from dust particles adhering to the slit.

The proper position of the tube with the slit with respect to the prism is usually fixed by the frame on which they rest. It must be so adjusted that the refracted rays pass through the prism as symmetrically as possible *i.e.*, in the minimum of their deviation, otherwise the spectrum will be less distinct and (owing to unequal refraction) will appear distorted. The symmetrical passage of the spectrum rays is approximately attained when the intermediate green rays pass through the prism symmetrically. Such a position must, therefore, be given the prism, with reference to the tube carrying the slit, that the middle green rays (line E of the sun spectrum) pass through it in the minimum of their deviation. It is then only necessary to so arrange the telescope that the green rays lie in the middle of the field of vision.

The *determination of the position of the lines of the spectra* is usually effected by means of a scale (see above). This arrangement is such (according to Bunsen) that the yellow sodium line coincides with the line 50 of the scale; then the red potassium line (α) will lie at 17, and the violet (β) at 152 (apparatus of Desaga). Since the refraction and dispersion of the rays are influenced by the quality of the glass of the prism, the scale indications of different forms of apparatus are not directly comparable. They must, therefore, be referred to an absolute measure.

This is most conveniently attained by reduction to the sun spectrum, which may be rendered visible in the telescope at the same time by means of a comparison-prism attached to the tube carrying the slit. We then determine the dark lines of the sun with which the lines of the flame under investigation coincide. In accurate determinations, the spectrum lines are represented in wave lengths, according to the millionth of a millimeter.

The apparatus described above is that usually employed in chemical laboratories. There are other forms adapted for special purposes—for investigation under the microscope, for the observation of the sun and stars. In accurate observations, where clear, broad spectra are required, the light is permitted to pass through several (3–9) prisms, consisting of hollow glass filled with carbon disulphide, which refracts light very strongly. Diffraction spectra may be advantageously applied in many instances in the place of the prism spectra.

The *direct line* (*à vision directe*) spectroscopes are very excellent for laboratory purposes. With these the spectra may be viewed in the direction in which the luminous objects really are; there are no deflections. This is accomplished by a combination of several prisms of crown and flint glass, whereby dispersion is attained, together with the simultaneous removal of deflection.

To observe the spectra of metals, it is only necessary, in many instances, *e. g.*, with the alkalies and alkaline earths, to introduce their volatile salts into a non-luminous alcohol or gas flame. A reduction of the metal usually takes place, and the spectra of the free metals themselves are obtained; thus, for example, sodium chloride is decomposed in the flame first into HCl and NaOH, which is then reduced by the carbon of the glowing gases to metallic sodium, and colors the flame yellow. The compounds difficult to decompose (as the barium salts), often afford independent spectra, differing from those of the free metal; this is plainly recognizable in the copper compounds.

Most metals, however, require a much higher temperature than that of the gas flame for their conversion into gases. To vaporize them and observe their spectra, the electric spark is made to pass from electrodes constructed of them. In this manner we can study all metals, even the most non-volatile, like gold, iron, and platinum. Their spectra are generally quite complicated, and exhibit a great number of single lines. Thus, over 450 lines have been established for iron.

Instead of making the electrodes of the metals we wish to study, we can, according to Bunsen (Poggend, Ann., 155), employ carbon points saturated with solutions of the metallic salts. A Ruhmkorf induction apparatus, with a dip battery of 4 elements, and an attached Leyden jar, will suffice to produce the electric spark. Such *spark spectra* are often quite different from the flame spectra obtained in gas flame.

A peculiar, very interesting and practical procedure for the production of spark spectra is due to Lecoq de Boisbaudran (*Spectres lumineux*, Paris, 1874). He allows the induction sparks to strike into the solution of the salt that is being examined. This is placed in a small reagent tube, in the bottom of which is fused a platinum wire. Above the surface of the liquid is the second electrode, a platinum wire connected with the positive pole of the induction spiral. The spectra of all the metals may be easily obtained by this contrivance, and, indeed, Lecoq de Boisbaudran discovered gallium by it.

The spectra of the elementary gases may be obtained by passing electric sparks through them; these will be variously colored. Hydrogen shines with a red light, which is decomposed and gives a spectrum consisting of a bright red, a blue, and a green line. Nitrogen shines with a violet light and affords a spectrum of many lines, chief of which are the violet. The spectra of gases may be more conveniently observed by aid of Geissler's tubes, which are filled with very dilute gases and the induction stream then passed through them.

These methods give us a means of readily distinguishing the individual chemical elements, and even detecting them in traces. Since the year 1860 various new elements, *e. g.*, cæsium, rubidium, thallium, indium, scandium, gallium, and several others, not accurately studied, have been discovered by their aid.

In addition to the direct, bright spectra just described there are yet *dark absorption spectra.* If a white light giving an uninterrupted spectrum be allowed to pass through different transparent bodies, the latter will absorb rays of definite refrangibility, allowing all others to pass. Therefore we observe the sun spectrum interrupted by dark lines or bands in the spectroscope. The solutions of didymium and erbium absorb certain rays, and show corresponding dark lines in the spectrum. The gases deport themselves similarly. White light that has traversed a broad layer of air shows in the spectrum several dark lines peculiar to nitrogen, oxygen, and steam. This power of absorption is possessed to a much higher degree by all incandescent gases or vapors. If a white light, like the Drummond calcium light, be conducted through the yellow sodium flame (through glowing sodium vapors), a dark line will appear in the rainbow spectrum of the white light, and its position will correspond exactly to that of the yellow sodium line; the latter thus appears converted into a dark line. If white light be passed through the potassium flame, two dark lines will be visible in the spectrum, corresponding to the red and blue lines of the potassium spectrum. Such spectra are designated the *inverted spectra* of the corresponding metals. The inverted spectra of all elements may be obtained in this way, and they correspond accurately to the direct bright spectra. The cause of these phenomena lies in the proposition deduced by Kirchhoff from the undulatory theory of light, *that the ratio between the emissive and absorptive power is the same for almost all bodies at like temperatures.* According to this, incandescent gases only absorb rays of just the same refrangibility as those which they emit. For example, when bright white light is passed through the yellow sodium flame the yellow rays of the former are absorbed and retained, while all others pass on almost entirely unaltered. Therefore, in the rainbow spectrum of white light the yellow rays of definite refrangibility will be absent; and if the other refracted rays of the white light are brighter than the yellow rays emitted from the sodium flame, the latter will be relatively darker; a dark line will therefore make its appearance.

These phenomena have presented a new and wide province to spectral analysis, inasmuch as they open up avenues for the investigation of the chemical nature of the sun and other bodies.

It is known that the bright rainbow sun spectrum is intersected by a number of dark lines which have been called the Frauenhofer lines from their discoverer. Kirchhoff has shown that these lines can be easily accounted for, after what has already been said, by the following hypothesis upon the nature of the sun: The latter consists of a solid or liquid luminous nucleus, surrounded by an atmosphere of incandescent gases and vapors. Then the uninterrupted spectrum of the glowing nucleus must be intersected by the dark lines of the inverted spectra of those gases and vapors which occur in the sun's atmosphere. An accurate comparison of the Frauenhofer lines with the spectrum lines of the various elements, has revealed the fact that iron, sodium, magnesium, calcium, chromium, nickel, barium, copper, zinc, and hydrogen are present in the sun's atmosphere. Thus dark lines have been found in the sun's spectrum corresponding to all of the 450 lines of the iron spectrum. The inferences upon the chemical constitution of the sun possess as much and, indeed, a higher degree of probability than falls to many other deductions.

The investigation of the sun's spectrum has cleared up many other changes occurring there, and this has led to a complete sun meteorology. All the fixed stars thus far investigated possess a constitution like that of the sun. They give spectra intersected by dark lines, and therefore consist of incandescent nuclei surrounded by gaseous atmospheres. The spectra of nebulæ, however, only show bright lines; hence these consist of uncondensed, incandescent masses of vapor.

Periodicity of the Spectrum Lines.—Since all other properties of the elements and their compounds have proved themselves to be periodic functions of the atomic weights, we may expect the same with reference to the spectrum phenomena. But few such regularities have occurred thus far. Most of the elements, especially the metalloids and the difficultly volatile metals, afford very complex spectra, which often vary at the same time with the temperature, so that spectra of 1st, 2d, etc., order are distinguished for some of them. It appears that not all spectral lines are of the same importance, since it has been possible, in some instances, to refer the various lines of a spectrum to particular fundamental lines whose relations to each other are comparable with those existing between the harmonics and the primary tones. Thus the four lines of the hydrogen spectrum may be looked upon as the harmonics of a single wave. Therefore, only individual lines are to be regarded in the comparison of spectra. This is clearly observed with the easily volatile metals belonging to the homologous groups, K, Rb, Cs; Ca, Sr, Ba; Ga, In, Tl; whose lines, lying in the violet portion of the spectrum, advance more towards the red end as the atomic weights increase; the wave lengths (in millionths of a millimeter) become successively greater with the increase of the latter or that of the atomic volumes:—

K	39	Wave	length,	404	Ca	40	Wave	length,	422
Rb	83	“	“	420.421	Sr	87	“	“	461
Cs	132	“	“	456.459	Ba	137	“	“	525.550

Ga	69	Wave	length,	403.417
In	113	“	“	410.450
Tl	209	“	“	535.

These relations are made apparent by the arrangement of the spectra in the spectrum plate.

A similar shifting of the spectral lines is observed with heterologous elements belonging to the same periods: K Ca, Rb Sr, Ba Cs, so that it seems possible to draw a conclusion upon the spectra of the succeeding elements. Indeed, the element scandium (45) succeeding calcium, shows intense violet lines of the wave length 425–440.

Heat of Formation of the Most Important Compounds of the Metals (according to J. Thomsen).

In usual state of aggregation (columns a), and in dilute aqueous solution (columns b).

	a	b		a	b		a	b
KCl	105.6	101.2	KBr	95.3	90.2	KI	80.1	75.0
$NaCl$	97.6	96.5	$NaBr$	85.7	85.6	NaI	69.1	70.3
$LiCl$	93.8	102.2	$LiBr$	...	91.3	LiI	...	76.1
$BaCl_3$	194.2	196.3	$BaBr_3$	169.4	174.4	BaI_2	...	144.0
$SrCl_2$	184.5	195.3	$SrBr_2$	157.7	173.8	SrI_2	...	143.3
$CaCl_2$	170.2	187.6	$CaBr_2$	141.2	165.7	CaI_2	107.6	135.3
$MgCl_2$	151.0	186.9	$MgBr_2$	...	165.0	MgI_2	...	134.6
$MnCl_3$	111.9	128.0	$MnBr_2$	...	105.1	MnI_2	...	75.7
$AlCl_3$	160.9	237.7	$AlBr_3$	129.6	204.9	AlI_3	70.3	159.3
$ZnCl_2$	97.2	112.8	$ZnBr_2$	75.9	90.9	ZnI_2	49.2	60.5
$CdCl_2$	93.2	96.2	$CdBr_3$	73.9	74.3	CdI_2	44.9	43.9
$FeCl_2$	82.0	99.9	$FeBr_3$	...	78.0	FeI_2	...	47.6
$CoCl_2$	76.4	94.8	$CoBr_3$	...	72.9	CoI_2	...	42.5
$NiCl_2$	74.0	93.7	$NiBr_2$	...	71.8	NiI_2	...	41.4
$FeCl_3$	96.0	127.7	$FeBr_3$	...	...	...	...	...
$SnCl_2$	80.8	81.1	$SnBr_2$	...	...	SnI_2	...	...
HCl	...	39.3	$TlBr$	41.4	...	TlI	30.1	...
$SnCl_4$	127.2	157.0	**HBr**	...	28.3	PbI_2	39.6	...
$TlCl$	48.5	38.4	$PbBr_2$	64.4	54.4	HgI_2	34.3	...
$PbCl_2$	82.7	75.9	$HgBr$	34.1	...	HgI	24.2	...
$HgCl$	41.2	...	$HgBr_2$	50.5	...	CuI	16.2	...
$HgCl_2$	63.1	59.8	$CuBr$	24.9	...	CuI_2	...	...
$CuCl$	32.8	...	$CuBr_2$	32.5	20.4	AgI	13.8	...
$CuCl_2$	51.6	62.7	$SbBr_3$	...	...	**HI**	...	13.1
$SbCl_3$	91.4	...	$AgBr$	27.7	...	TlI_3	...	10.5
$BiCl_3$	90.6	...	$TlBr_3$	...	56.1	AsI_3	12.6	...
$AgCl$	29.3	...	$AsBr_3$	47.1	...	AuI	—5.5	...
$AsCl_3$	71.4	...	**HBr**	8.4	...	**HI**	—6.0	...
$TiCl_3$	...	89.0	$AuBr$	—0.1	...	PtI_2	..	...
HCl	22.0	...	$AuBr_3$	8.8	5.0			
$AuCl$	5.8	...	$PtBr_3$	...	...			
$AuCl_3$	22.8	27.2						
$PtCl_2$	...	...						

	a	b
KOH	103.9	116.4
$NaOH$	102.0	111.8
$LiOH$	...	117.4
BaO_2H_2	216.3	226.6
SrO_2H_2	216.4	226.1
CaO_2H_2	214.7	217.8
MgO_2H_2	217.2	...
AlO_3H_3	296.9	...
MnO, H_2O	94.7	...
ZnO, H_2O	82.6	...
H_2O (liquid)	68.3	
FeO, H_2O	68.2	...
$Fe_2O_3 . 3H_2O$	191.1	...
CdO, H_2O	65.6	...
CoO, H_2O	63.4	...
NiO, H_2O	60.8	...
SnO, H_2O	68.1	...
SnO_2, H_2O	133.5	...
H_2O (vapor)	58.0	
PbO	50.3	...
As_2O_3	154.6	147.0
Tl_2O	42.2	39.2
HgO	30.6	...
Hg_2O	42.2	...
CuO	37.1	...
Cu_2O	40.8	...
$Tl_2O_3 . 3H_2O$	86.0	...
PdO, H_2O	22.7	...
Ag_2O	5.9	...
$Au_2O_3 . 3H_2O$	—13.2	...
Li_2O	...	166.5
K_2O	(99.1)*	164.5
Na_2O	(100.2)	155.2
BaO	130.4	158.2
SrO	130.9	157.7
CaO	131.7	149.4

	a	b
KSH	(64)†	65.1
$NaSH$	(55)	60.4
$LiSH$	...	66.0
BaS_3H_2	...	124.1
SrH_2S_2	...	123.6
CaS_2H_2	...	115.3
MgS_2H_2	...	114.8
MnS, nH_2O	46.3	...
ZnS, nH_2O	41.5	...
CdS, nH_2O	33.9	...
FeS, nH_2O	23.7	...
CoS, nH_2O	21.7	...
NiS, nH_2O	19.3	...
Tl_2S	21.6	...
PbS	20.4	...
CuS	10.0	...
Cu_2S	20.2	...
HgS	16.8	...
Ag_2S	5.3	...
H_2S	4.5	9.2
K_2S	102.4†	113.2
Na_2S	(88.4)	103.9
Li_2S	...	115.2
BaS	(99.0)	107.1
SrS	(99.2)	106.6
CaS	(92.0)	98.3
MgS	(79.6)	(110)
Al_2S_3	(124.4)	...

	a	b
K_2SO_4	344.5	337.2
Na_2SO_4	328.5	329.0
Li_2SO_4	334.1	340.1
$BaSO_4$	337.5	...
$SrSO_4$	320.8	...
$CaSO_4$	319.9	...
$MgSO_4$	302.2	323.0
$Al_2S_3O_{12}$	...	878.9
$MnSO_4$	249.8	263.5
$ZnSO_4$	230.0	248.4
$CdSO_4$	221.1	231.8
$FeSO_4$	...	235.6
$CoSO_4$	...	230.4
$NiSO_4$	...	229.3
Tl_2SO_4	221.0	212.7
H_2SO_4		210.7
$PbSO_4$	216.2	...
H_3SO_4	192.9	
$CuSO_4$	182.5	198.3
Ag_3SO_4	167.2	162.7
K_2CO_3	279.5	286.0
Na_2CO_3	271.0	276.5
$BaCO_3$	281.3	
$SrCO_3$	279.6	
$CaCO_3$	269.2	
$MnCO_3$	209.2	
$CdCO_3$	179.9	
$PbCO_3$	168.2	
Ag_3CO_3	121.3	

	a	b
KNO_3	119.4	111.4
$NaNO_3$	111.2	106.2
$LiNO_3$	111.6	112.2
BaN_2O_6	225.7	216.3
SrN_2O_6	219.8	215.2
CaN_2O_6	203.2	207.1
MgN_2O_6	...	206.3
MnN_3O_6	...	147.5
ZnN_2O_6	...	132.3
CdN_2O_6	...	115.8
FeN_2O_6	...	119.5
CoN_2O_6	...	114.3
NiN_2O_6	...	113.2
HNO_3		49.1
PbN_2O_6	105.5	97.9
$TlNO_3$	58.1	48.1
HNO_3	41.5	...
CuN_2O_6	...	82.2
$HgNO_3$	...	38.9
HgN_3O_6	...	67.1
$AgNO_3$	28.7	23.3

* According to Beketoff.

† According to Sabatier.

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